

1936

# The effect of phosphate fertilizers on soil reaction

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THE EFFECT OF PHOSPHATE FERTILIZERS ON SOIL REACTION

BY

John Booth Peterson

A Thesis Submitted to the Graduate Faculty  
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject Soil Fertility

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## INTRODUCTION

Farmers for many years have recognized the existence of an undesirable soil condition which could be remedied by applying lime. Even today soil acidity is expressed in terms of lime requirement and often defined as "that condition of the soil which can be remedied by the application of lime."

Since 1800 a growing volume of research dealing with the phenomenon of soil acidity has yielded an abundance of valuable information but many questions remain incompletely answered. This has been due to some extent to a lack of appreciation of the breadth and scope of the problem. More work has been done on the value of lime, on comparisons of the effectiveness of different kinds of lime and of different degrees of fineness, on ways of applying lime and on similar studies than has been done on the more basic questions of why acidity is deleterious to some plants and why lime has the ability to remedy this condition.

The optimum soil reaction may vary with different species of plants, with different soil types and even with changes within the soil type itself. Because of this there has been considerable lack of agreement in the results of tests of the lime requirements of various plants.

Ecologists differ in their conclusions regarding the importance of acidity in determining plant distribution. The question is continually raised as to whether reaction is very important or whether incidental phenomena such as the supply of

calcium for plant nutrition or the increased solubility of toxic aluminum in acid soils are not more important.

The results of laboratory and field experiments have convinced most agronomists of the value of lime in a sound, long-time agricultural program. The adoption of a "sweet soil" system of agriculture as a basis for permanent soil fertility has been sponsored by several agricultural experiment stations including those of Iowa and Illinois and has been generally accepted throughout the United States. Except for those types of agriculture which require acid soils because of the preference of one or more of the main cash crops for acidity, there is a predominance of evidence in favor of a "sweet soil" system. The fact that many of the most efficient soil building rotations are built around "lime-loving" legumes, that nitrogen fixing bacteria and most of the other beneficial forms of soil microorganisms are more efficient in neutral soils, that plant food nutrients are more available near the neutral point and that lime has a direct beneficial effect on the physical properties of the soil all justify the use of lime on acid soils.

When it is realized that all the soils of the United States east of the western boundary of the prairies belong to the major soil group of Pedalfers, that is, soils which lack the presence of a zone of lime carbonate accumulation in some horizon or layer of the soil profile, and which are fundamentally acid because of the absence of a reserve supply of basic salts, the importance of mineral fertilizers which have an alkaline effect is apparent.

Some of the commonly used fertilizers have a marked alkaline residual effect on the soil and their promoters have not passed up the opportunity to point out the value of such materials on acid soils. Among these fertilizers are such materials as basic slag containing 40 to 50 per cent of calcium and magnesium compounds largely in the form of oxides; calcium cyanamide, advertised as containing 75 per cent hydrated-lime equivalent as well as 22 per cent nitrogen; sodium nitrate which, according to Van Slyke (90), will save the soil one pound of calcium carbonate for each pound applied; calcium nitrate and others.

Potassium chloride, ammonium sulfate, sulfur and gypsum are known for their tendency to increase soil acidity.

The effect of certain of the phosphate fertilizers on the reaction of the soil has not been so marked. When Lawes first began acidulating phosphate rock about one hundred years ago he called his product "superphosphate". Later the name "acid phosphate" came to be applied to any rock phosphate conditioned with sulfuric acid. Since this name seemed to imply that acid phosphates made the soil acid, a point over which there is some difference of opinion, the fertilizer trade has recently gone back to the old name of "superphosphate".

Considerable evidence may be found of the beneficial effect of rock phosphate on acid soils. In fact, it seems possible in view of some of the data reported in the last few years that rock phosphate may partially supply the need for calcium, at least in some cases. In the past few years an advertisement for a finely

ground rock phosphate has appeared which reads, "Fertilize with Ruhm's Lime Phosphate, the economic source of phosphorus, calcium for nothing."

With the growing demand for the ammoniated phosphates such as leunaphos, ammo-phos and leunaphoska the question is raised as to the probable residual effect of such materials on the reaction of the soil. Some agronomists point out that the continued use of these fertilizers might be expected to increase acidity.

With the exception of basic slag the effect of different phosphate fertilizers on soil reaction is probably small. This fact, together with the variability in results for the same fertilizer on different soils, explains why there is a general lack of agreement in the data showing the effect of superphosphate, rock phosphate and the ammoniated phosphates on soil reaction.

This study was outlined with the purpose of obtaining more specific information on the effect of certain phosphate fertilizers on the reaction of some of the acid soils of Iowa.

## HISTORICAL

### Soil Acidity

A notable example of the early application of alkaline earths occurred in prehistoric Aegina where their use became a theme of mythology. On this small densely populated island the surface stratum of poor fresh-water limestone was underlaid by a stratum of fertile marl.

Sampele (69) tells how the inhabitants pierced the sterile veneer, dug out the marl and mixed it with the soil above to produce crops. This habit of burrowing underground and using the excavations for dwellings fastened on the Aeginetans the name of Myrmedons or ants.

The Romans imitated the practice of the Greeks and Gauls in the use of marl. They distinguished several varieties and applied them to grain and meadow lands. It is not known when man first began using marls and ashes to sweeten sour soils but such use has been an established agricultural practice for ages. It is only natural that acidity should be expressed in terms of lime requirement.

Lime requirement, however, is only a relative term, being constant neither for soil nor plant. One of the interesting papers emphasizing the complexity of the problem is that of Pryanishnikov (63) who pointed out that each soil behaved differently. Mustard plants did not grow at a pH of 4.5 on a sandy soil but grew well on a loam soil of similar reaction.

Peas did best on a slightly alkaline soil but the yield on a chernozem of pH 4.5 was 85 per cent as great as on the alkaline soil. He concluded that soils of a higher buffer capacity are capable of supporting plants at a low pH. He also found that changing the source of nitrogen shifted the optimum pH for plants. Sugar beets grew best with ammonia as a source of nitrogen at a pH of 7 but with sodium nitrate they grew best at a pH of 5.5. The intake of calcium seemed to be hindered by the use of ammonia as a source of nitrogen.

Another study emphasizing the complexity of the problem is that of Emmert (25) who found that soil reaction changes were not so important to the growth and yield of tomatoes as the indirect effects on nutritional relationships and on toxicity of the soil. In his work the materials added to change the pH of the soil exerted different effects on the crops. For example, soils with a pH of 8.3 to 8.5 produced by sodium carbonate gave higher yields of tomatoes than did soils at the same pH produced by calcium carbonate. A large increase in the yield of lettuce was produced by making a soil acid to pH 5.4 to 5.6 with phosphoric acid. Also pH of 6.0 to 6.5 with sulfuric acid produced increases in the yield of lettuce. Yet, surprisingly enough, a large increase could be obtained by raising the pH of the soil to 7.2 with sodium carbonate.

Emmert (25) also found that lime without organic matter caused poor growth and yellow foliage of both tomatoes and lettuce.

Albrecht (3) called attention to inconsistencies in reaction

ranges tolerated by plants when other factors in the environmental conditions varied. All this emphasizes that lime requirement is specific for a certain plant on a certain soil, and, one might add, under a given management and manurial treatment. Nevertheless, there is good evidence that different plant groups do prefer in general certain ranges of soil reaction. Probably the best known example is the preference of certain legumes for neutral soils. Some plants have a broad range, others but a narrow range of preference. The narrower the range of optimum reaction, the more important is the lime requirement problem for that plant.

The benefits of lime as described in such soil texts as those of Van Slyke (90) and Lyon and Buckman (47) may be traced to its neutralizing effect on soil acidity, to the nutritional value of the calcium supplied and to its favorable physical influence on the soil.

While the functions of lime are fairly well defined, the residual effects of many mineral fertilizers are not so easily predicted. There are those which have a marked alkaline effect, some that decidedly increase soil acidity and others whose effects are so slight and easily modified by variations in soil and crop as to be difficult to measure and hence are little understood. Most of the phosphate fertilizers belong in this latter group.

Delivering the presidential address before the twenty-fifth annual meeting of the American Society of Agronomy in 1932, Brown



(15) said of this problem, "In connection with phosphorus fertilization, I may also mention the problem of the effect of phosphorus carriers on the reaction of the soil and its need of lime. What changes in reaction, if any, are brought about by different phosphorus fertilizers? Do they have any neutralizing effect on acidity? There has been much talk of such an effect but little evidence. Now, we believe little or no neutralizing effect on acidity can be expected from phosphate additions. But future investigations may lead us to change our views."

#### The Importance of Calcium in Phosphate

If rock phosphate can take the place of lime to some extent on acid soils, it may do so in one of two ways. It may supply calcium as a plant nutrient and it may neutralize some of the soil acidity. Because of the difficulty of separating the nutritional effects of lime from its neutralizing power, investigators have been doubtful as to the relative importance of these two functions. The fact that sometimes supposedly "lime-loving" plants were found growing luxuriantly in soils which, although acid, contained a supply of soluble calcium, raised the question of the actual importance of soil reaction in plant growth.

Speaking of conditions in Iowa, Brown (15) said, "We know that liming benefits the growth of legumes on most acid soils. But some legumes grow well on certain acid soils and not on others."

Robinson and Williams (65) claim that in many cases un-

saturation does not of necessity mean low fertility as long as there is plenty of exchangeable calcium present in the soil.

Albrecht (2) concluded that the common failure of legumes on acid soils has led to the belief that the soil acidity was responsible. He recommended further consideration of the question whether legume failure was caused by the harmful effects of soil acidity or by failure of plants to obtain sufficient calcium. He felt that because increased deficiency of calcium usually paralleled excessive degrees of acidity, as found by Swanson et al (77), the two possible causes of legume failure had not been adequately differentiated.

Albrecht (2) tried the effect on soy bean inoculation of two larger amounts of calcium at one hydrogen ion concentration. He found the higherrate to be more beneficial to nodulation. From this he concluded that the significance of calcium for soy bean plants rested on its function as an element in the plant's activities rather than on that of reducing the hydrogen ion concentration of the growth medium.

Later Albrecht (3) described soil acidity as representing (a) an environmental condition in which excessive hydrogen ion concentration is intolerable and (b) an irregularity in nutrition of the plant, possibly through shortage of basic elements replaced by the hydrogen or through injury to, or destruction of, the plant's mechanism for adsorption and utilization of the necessary nutrient elements. He found that the degree of acidity was responsible for nodulation failure on excessively acid soils,

whereas, on soils with a pH above 5.0 the deficiency of available calcium in the soil was a more important factor.

Whitson and Chapman (93) claimed that available lime frequently exists in soils in considerable amounts even though the soil is acid. For this reason they believed it was important to determine directly the amount of available lime in a particular soil rather than simply the acidity. They stated that acidity itself was apparently seldom the cause of failure of alfalfa in Wisconsin when there was enough available calcium, phosphorus and potassium present in the soil.

In 1929 Whitson, Chapman and Hull (94) found that alfalfa, clovers and other "lime-loving" farm crops did not need a sweet or alkaline soil so much as they needed an available supply of calcium. They found that soil acidity, as such, was not particularly detrimental if adequate supplies of calcium were available. They claimed that many acid soils produced good alfalfa and upon testing some of those soils found an average of 565 pounds of available calcium per acre. Soils of the same degree of acidity, but producing poor alfalfa, averaged but 346 pounds per acre of available calcium.

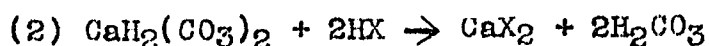
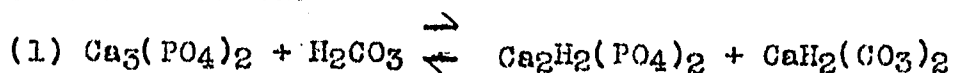
Albrecht (1) followed up his work on calcium with field tests of the value of small amounts of fine lime drilled in the row. He reported good results with clover and attributed it to "some effects, not dependent entirely on complete neutralization but probably connected with the solubility of calcium."

Salter (66) reported superior results from drilling small

amounts of either pulverized limestone or hydrated lime with clover and alfalfa seed than with larger applications of lime broadcasted in the spring. However, when applied in the fall broadcasted limestone was the best.

#### The Solubility of Calcium in Phosphate Rock

If some phosphate fertilizers may be substituted for lime, they may do so by supplying calcium to the plant. If this is the case, it is fair to ask how the calcium gets into solution. Truog (83) in discussing the effect of reaction on the availability of phosphate in the soil, claimed that in case of applications of insoluble phosphates the acidity of the soil increased the availability of the phosphorus, at least for several years, and gave the following equations illustrating the reactions involved:



He also claimed that in case of the application of rock phosphate to neutral or basic soils the soil solution became saturated with calcium bicarbonate, thus permitting very little acid action on the particles of rock phosphate. When rock phosphate was used on an acid soil, there was a fairly rapid change of the phosphate to iron and aluminum phosphate which he believed was much more available than the original rock phosphate because of better distribution of the precipitated material.

According to Truog (83) the order of availability of phosphate compounds was

1. Precipitated tricalcium phosphate.
2. Precipitated iron and aluminum phosphate.
3. Rock phosphate particles (200 mesh).
4. Crystalline iron and aluminum phosphate.

From this he estimated that superphosphate would go into solution on both basic and acid soils giving best results on basic soils because it would be precipitated as tricalcium phosphate.

In explaining the feeding power of plants for phosphate rock Bauer (10) pointed out that acids secreted by roots were first thought to be very important. Later when it was found that the only acid secreted by roots, carbonic acid, did not seem to have much relation to the feeding power of plants, the solution of phosphates was said to depend on acids resulting from the decay of organic matter in the soil. Although only small amounts of water-soluble phosphorus resulted from additions of organic matter, Bauer (10) pointed out that good response to rock phosphate was usually obtained when organic matter was plowed under. He thought that plants used the small amounts of soluble phosphate formed, thus unbalancing the equilibrium so that by the law of mass action more phosphorus would come into solution. He wrote the reaction explaining the solubility of the rock phosphate as



He believed that plants which assimilated large amounts of

calcium would be high phosphorus feeders because they would help to keep the excess calcium removed, thus permitting more phosphorus to come into solution. For the same reason Truog (82) thought plants containing a high CaO content would be efficient users of rock phosphate.

McGeorge (48) showed that even in calcareous soils carbon dioxide secreted by the roots was able to make phosphates available by producing the necessary degree of acidity at the point of root contact. He found that plants have a decided preference for phosphorus as  $\text{H}_2\text{PO}_4$  which is the dominant ion at slightly acid reactions.

In an article published in 1930 Truog (85) indicated that an abundance of lime helped to keep the phosphate "tied up" with calcium in the form of readily available calcium phosphate.

Thor (73) quoted Truog as saying that a pH of 6.5 or higher is necessary to keep a considerable portion of phosphorus in available form and that most agricultural crops grow best in the pH range 6.5 to 7.5. Thor concluded that most agricultural crops could utilize rock phosphate to greater advantage in slightly acid soils.

The importance of soil reaction on the solubility of phosphates was shown by Truog (87) in tests which showed that a pH of 6.2 was too acid for best use of phosphates by plants. This was attributed to the low availability of Goethite ( $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) believed to form when phosphate is added to soils more acid than pH 6.5.

Further studies in phosphate fixation as a factor in the solubility of the phosphate were made by Ford (26) who gave the following order of availability for phosphates fixed in the soil:

Calcium and magnesium phosphates	- most available
Iron and aluminum phosphates (from relatively soluble iron and aluminum compounds)	- intermediate availability
Phosphate from limonite	- low availability.

From the foregoing discussion it is apparent that phosphates react with acids when present in the soil or excreted from roots to form calcium salts of the acid anhydrides and more or less soluble phosphate salts. Reaction of the soil and the presence or lack of calcium carbonate are important in determining the rate at which the phosphate is dissolved and the completeness of its solution. If the law of mass action controls these reactions as believed by Truog (83), Bauer (10) and others, excessive amounts of lime may be expected to retard the reaction and keep the calcium and the phosphate from coming into solution until some of the calcium salts so formed are removed. On the other hand, if the soil is too acid, iron and aluminum phosphates are formed, which, according to Truog (83), Ford (26) and others are less soluble than calcium and magnesium carbonates.

A rather complete review of the literature on phosphate fixation in soils is presented by Ford (26) and by Obenshain (53).

Ford (26) found that hematite had a low fixing power for phosphate, whereas, limonite had a high fixing power. Of the phosphates fixed by the soil he found calcium and magnesium

phosphates the most available, iron and aluminum phosphates formed from relatively soluble iron and aluminum compounds intermediate, and the phosphate formed from limonite quite slowly soluble. Even in the process in which phosphates are fixed as iron or aluminum phosphates in acid soils, the calcium of the original phosphate must neutralize some of the soil acidity as shown by Truog (83).

Other soil factors affect the solubility of rock phosphate such as differences in texture, structure, organic content, moisture relationships, and microbiological activity. The chemical composition of the phosphate applied and its physical properties, especially degree of fineness, are important. These factors are well known and are described in several soil texts, such as that of Van Slyke (80) and need no further elaboration here, with the possible exception of some of the later ideas concerning the composition of rock phosphate and the effect of magnesium on phosphate solubility.

It has been customary to speak of rock phosphate as tricalcium phosphate as Jacob (37) and Buie (16) have pointed out. According to these men tricalcium phosphate rarely occurs in nature and X-ray investigations have shown that tricalcium phosphate and phosphate rock are different chemical compounds. Phosphorus is present in rock phosphate principally as a complex compound of calcium phosphate and calcium fluoride having the empirical formula  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ .

Truffaut and Bezssonoff (80) concluded that the low avail-



ability of rock phosphate as compared with tricalcium phosphate was due to a protective mechanical action of the fluoride and extremely low availability of the fluoride-triphosphate complex.

Marshall et al (50) reported that the analysis of 137 samples from 34 localities indicated that fluorine is almost invariably present in phosphate rock in quantities ranging from 0.40 to 4.25 per cent of the sample. It was found that continental deposits were generally high in fluorine, whereas, island deposits were generally low.

Phillips et al (57) found that 1000 pounds of rock phosphate added 35 pounds of fluorine to the soil and a like amount of superphosphate added half as much. Not enough fluorine was taken up by crops on heavily phosphated fields to be detrimental to animals feeding there but enough appeared in the drainage water from such fields to be harmful to animals drinking it.

Bartholomew (8) found a significant correlation between the amount of fluorine absorbed by the plant and the amount applied in rock phosphate and (9) later found that the presence of chemically combined fluorine in phosphate rock greatly decreased the availability of the phosphorus to plants. As the amount of fluorine was increased the availability of the phosphate was lessened.

Another factor important in the solubility of phosphate in the soil but not generally considered until recently is the amount of replaceable magnesium in the soil, according to Truog (86) and Loew (46).

Additional evidence of the value of magnesium in making phosphorus more available to plants was found by Thor (78) and Kellogg (42). Kellogg (42) concluded that the crop increase obtained with superphosphate or with sulfur was the result of an increased solubility of magnesium following the use of sulfur or gypsum. The repressive effect of calcium carbonate on the availability of magnesium was thought to be a cause of low response to phosphate on high-lime soils. Later work by Truog and Hill (89) confirmed these findings.

Data secured by Pierre and Browning (61) showed that substitution of increased amounts of magnesium carbonate for calcium carbonate up to 75 per cent improved growth and produced normal leaf color of plants. The use of magnesium carbonate materially increased the water-soluble  $P_2O_5$  of the soil solution.

The foregoing review shows that ordinary phosphates used as fertilizers yield calcium to react with the acids in the soil. Evidence of this was supplied by Truog and Cook (88) who demonstrated that so-called base-exchange acids isolated from soils and bentonites helped to make the phosphorus of phosphate rock available to plants. This also showed that there were acids in the soil which would react with calcium phosphates. Theoretically, there is no reason why calcium phosphates should not have some neutralizing effect on soil acidity.

The Effect of Phosphate Fertilizers on Soil  
Reaction

Bauer (10) claimed that the availability of phosphate depended on the laws of mass action and chemical equilibrium. Plants that used calcium as well as phosphorus from rock phosphate were good phosphate feeders. He concluded that on many soils of slight or moderate acidity the calcium of phosphate rock was sufficient to supply the needs of some legumes, such as red and mammoth clover. If the soil were too acid, lime also would have to be applied, but not excessively. He was of the opinion that rock phosphate could not supply enough calcium for the needs of sweet clover or alfalfa on acid soils because the needs of these two plants for calcium is so great that unless the soil is practically neutral limestone must be applied.

Later Bauer (11) concluded that the calcium of rock phosphate could not be considered as a substitute for limestone in growing clover except in a limited sense. He thought the amount of calcium that could be derived from rock phosphate would be insufficient and too slowly available on most soils which were too acid to grow clover.

Thor (78) found some indications on the Hopkins' farm in Illinois that applications of rock phosphate had reduced soil acidity slightly.

DeTurk (24) showed that the superior ability of alsike clover to thrive on an acid soil was at least partly the result of its ability to obtain and use large amounts of both calcium

and phosphorus from the comparatively unavailable form in which these elements occur in acid soils. The alsike clover also apparently moved the calcium and phosphorus within the plant with greater facility than did alfalfa. Although this would seem to be a point in favor of the ability of calcium phosphates to partially substitute for lime on acid soils, DeTurk concluded that acid soils adequately fertilized with rock phosphate would also need lime.

Lauder and Smith (45) found that successive additions of a 26 per cent mineral phosphate to aqueous suspensions of a clay loam up to five per cent produced a regular increase in pH up to 7.7. With a sandy loam a maximum addition of 4 per cent mineral phosphate increased the pH from 4.97 to 6.76 and with a peat soil an addition of 9.0 per cent mineral phosphate increased the pH from 3.69 to 5.3.

Snider (76) found that rock phosphate applied with potash and three tons of limestone raised the pH from 6.0 to 6.2 after 27 years of treatment on the Odin experiment field in Illinois. Where six tons of limestone were used, no increase in pH resulted with the rock phosphate.

Hopkins and Whiting (35) introduced some ammonium sulfate and nitrifying organisms in a sterile flask containing some phosphate rock as a means of determining the extent to which the acids produced acted on the rock phosphate. The average results from 13 duplicate trials showed that 115 pounds of phosphorus and 211 pounds of calcium were found in solution for every 56 pounds

of nitrogen changed from the ammonia form to the nitrite form. Approximately 90 per cent of the phosphate rock was dissolved. They concluded that nitrification resulted in solubility of calcium and phosphorus from rock phosphate, the solubility increasing with increased time of action of the bacteria.

Seuey (72) compared the solubility of limestone and rock phosphate in one per cent and two per cent solutions of nitric acid and found that the rock phosphate was more soluble than the limestone at both strengths.

Burgess (17) measured the pH of the soil on old fertility plots at four different dates and found that rock phosphate increased the pH although not as much as did superphosphate. He also found that the rock phosphate increased the acidity of the soil according to the Jones lime requirement method.

Hance (28) and Smith (75) did not find differences in reaction of the soil following the use of rock phosphate.

Conner (21) treated an acid clay soil and an acid peat soil with different phosphatic materials in equivalent amounts of phosphoric acid. The amount was based on an application of 8,000 pounds of superphosphate per 2,000,000 pounds of soil. The rock phosphate reduced the acidity of both soils as measured by the normal potassium nitrate method.

The results of researches on the effect of superphosphate on soil reaction have been equally as varied as have those on the effect of rock phosphate.

As early as 1915 Conner (21) reported that when phosphates were added as fertilizer to acid soils, even in the form of acid phosphate, the soluble phosphate was soon fixed and no increase in acidity occurred. He also reported that on experimental plots at the Purdue Experiment Station, soils treated for twenty years with acid phosphate showed less soluble acidity than untreated soils. Acid soils and silicates treated in the laboratory with acid phosphate showed less soluble acidity than untreated soils and silicates. In these last named studies other phosphorus compounds were used. The following table gives an idea of the comparative neutralizing value of the different materials measured by the normal potassium nitrate method on an acid peat soil, "D" and an acid clay soil, "K".

Results on 25 gm. soil digested with 250 cc. N.  $\text{KNO}_3$

<u>Treatment of Sample</u>	<u>Acidity</u>	
	<u>Pounds <math>\text{CaCO}_3</math> per million</u>	
	<u>D</u>	<u>K</u>
None.....	4,000	4,040
0.0125 gm. phosphoric acid.....	3,840	3,960
0.024 gm. monocalcium phosphate.....	3,760	3,720
0.034 gm. dicalcium phosphate.....	3,600	3,120
0.03 gm. tricalcium phosphate.....	3,520	3,240
0.10 gm. acid phosphate.....	3,840	3,840
0.05 gm. raw rock phosphate.....	3,760	3,800

It is significant that increases in the amount of calcium in the molecule of the pure calcium phosphate resulted in decreases in acidity. Acid phosphate and phosphoric acid both decreased acidity by the same amount. Rock phosphate was more effective in neutralizing acidity than was the acid phosphate.

In a review of the literature on the effect of acid phosphate

on soil acidity Burgess (17) emphasized the difference of opinion existing as to the effect of the more soluble phosphates on soil reaction. He pointed out that although the majority of writers stated that acid phosphates did not permanently increase soil acidity and upon certain types of soil might slightly reduce it, there were those who contended that acid phosphate increased the capacity of the soil for lime absorption. Burgess was inclined to discredit the work of those who found an acidic effect resulting from acid phosphate. From the results of pH determinations of samples taken from long-time fertility plots he concluded that Thomas slag, acid phosphate, ground bone, floats (rock phosphate) and double superphosphate all tended to reduce soil acidity somewhat. He claimed that there was no foundation for the statement that soils would become acid from the continuous use of acid phosphate.

Among other investigators who have reported a neutralizing effect from superphosphate may be listed Harrison (32) who found a slight decrease in acidity following the application of large amounts of superphosphate over an extended period.

Some recent investigators who have found no change in soil reaction when superphosphate was applied are Jensen (33), Pittman (62), Hance (28) and Joret (39).

There are a number of workers who have found that soil acidity increased with additions of superphosphate. Lauder and Smith (45) found that additions of superphosphate, incorporated with the soil and shaken daily over a period of three months re-

duced the pH of a clay loam but did not appreciably change the reaction of a sandy loam or of a peat soil.

Snider (76) found that after 27 years of treatment the plots of the Odin field of Illinois which had received a total of 7000 pounds of superphosphate and the equivalent of approximately 400 pounds an acre of elemental potassium were more acid in reaction than was the soil of the check plot which was similarly treated except for the superphosphate. This was true whether the basic treatment for these plots was three or eight tons of limestone per acre.

Skinner and Beattie (73) found that acid phosphate treated soils became more acid than untreated soils but not so acid as the soils treated with potassium sulphate. They observed the disagreement between their findings and those of Conner (21) who reported decreased acidity after twenty years of fertilization with superphosphate. They also found that calcium sulphate increased the acidity of an acid Arlington silty clay loam.

Superphosphate reduced the degree of acidity of the soil under investigation according to Sewell and Latshaw (70), but this reduction lasted only a short time. Subsequent determinations made several months later showed that the superphosphate soils had about the same reaction as the untreated soils.

Pierre (60) studied the effect of different phosphate materials and lime on the pH of three soils, one of slight acidity, one medium and one very acid. He compared mono-, di-, and tricalcium phosphates, monosodium phosphate, superphosphate



and rock phosphate. All the phosphates studied caused decreases in the acidity of the very acid soil. Dicalcium phosphate, tricalcium phosphate, and monosodium phosphate caused the greatest decreases, while monocalcium phosphate, superphosphate and rock phosphate caused relatively slight decreases in acidity. With the medium acid soil dicalcium, monosodium, and tricalcium phosphate decreased acidity, although not to so large an extent as with the very acid soil. On this soil, however, monocalcium phosphate caused no decrease in soil acidity and superphosphate caused a slight increase in acidity as shown by pH values. With the slightly acid soil tricalcium and dicalcium phosphate showed slight decreases in acidity but monocalcium phosphate caused a slight increase and superphosphate a large increase in acidity. These results showed that the original reaction of the soil influenced the effect of the various phosphates on soil reaction: the more acid the soil, the greater the basic action of the different phosphates or the less their acidic effect.

Treble superphosphate may be regarded as ordinary superphosphate from which the gypsum has been removed. It usually contains from two and one-half to three times as much available phosphoric acid as does the ordinary superphosphate. Practically all the phosphorus is in the form of monocalcium phosphate. As was the case with superphosphate and rock phosphate, treble superphosphate has been found to neutralize the acidity of the soil in some cases, to increase acidity slightly or to cause no change in reaction in other cases. Conner (21) found monocalcium

phosphate reduced the acidity of the soil but not as much as did dicalcium or tricalcium phosphate. Hance (28) and Pittman (62) noted no change in reaction following the use of treble superphosphate. Pierre (60) found that monocalcium phosphate decreased acidity on a highly acid soil, caused no appreciable change in reaction on a medium acid soil and increased acidity somewhat in a slightly acid soil although by a much smaller amount than did superphosphate. He attributed the difference in effect between these two materials to the presence of gypsum in the superphosphate.

Pierre (59) based the neutralizing value of rock phosphate in fertilizer mixtures on the amount of citrate-insoluble phosphoric acid in the fertilizer mixture. At first he assumed that rock phosphate was basic in its effect to the extent of whatever carbonate impurities were present plus two-thirds of its calcium in the form of phosphate. Subsequently he decided that the rate of solution of phosphate rock was too slow to permit its being given full credit for neutralizing purposes. On the former basis Florida rock phosphate used for filler-substitute purposes would have a neutralizing value equivalent to that of 805 pounds calcium carbonate equivalent per ton. On the new basis this would be reduced to 240 pounds calcium carbonate equivalent per ton.

According to the American Cyanamid Company (6) phosphate rock has value in the soil as a carrier of both lime and phosphoric acid. It was claimed that in the light of past experi-

ments phosphate rock was known to be quite an effective fertilizer on acid soils. It was also pointed out that phosphate rock had a solubility greater than that of dolomitic limestone in weak acid solutions; that the crop-producing power of mixtures containing these two materials in the amounts required by the original Pierre (59) method are similar and that the effects of such mixtures on the soil reaction are practically identical. Because of this The American Cyanamid Company (6) recommended that Pierre's first suggestion for calculating the neutralizing value of rock phosphate in fertilizer mixtures be used.

While considering the neutralizing value of phosphates as basic material in mixed fertilizers it is well to keep in mind the difference between the physiological acidity of fertilizers and the acidity of soils. This is pointed out by Shuey (72) who also said that soil acidity so high as to reduce the yields of crops should be corrected by liming, the amount depending on the degree of acidity. The neutralizing power of certain basic materials in respect to the free acids and acid salts present in fertilizers should not be confused with their ability to neutralize soil acidity.

The effect of ammoniated phosphate on soil reaction must be the result of the combined effects of the ammonia compounds and the dicalcium and monocalcium phosphates. Pierre (60) found that the effects of these two phosphates on reaction varied from none to a distinct neutralizing effect, depending on the original acidity of the soil.

Conner (21) found that dicalcium phosphate and tricalcium phosphate had a greater neutralizing effect on the soil than did superphosphate, rock phosphate, phosphoric acid or monocalcium phosphate.

Pierre (58) studied the effect of different nitrogen fertilizers on soil acidity and reported that sodium nitrate, calcium nitrate, and calcium cyanamid decreased acidity, whereas, ammonium sulfate, ammonium phosphate, leunasalt peter, urea, and ammonium nitrate caused an increase in acidity. He used the results of exchangeable hydrogen studies to prepare a table giving the proportions of different nitrogen fertilizers to use in building various fertilizer combinations which would not change the original reaction of the soil. He claimed that a combination of 70 per cent nitrogen in the form of sodium nitrate and 30 per cent in the form of ammonium sulfate could be used without affecting the soil reaction. He believed that calcium nitrate could be substituted for sodium nitrate since it had about the same reaction. Similarly, in all his combinations, he recommended the substitution of ammonium phosphate for ammonium sulfate in equal amounts.

Allison (5) reported also data which showed that the acidic effects of the use of one pound of ammonium sulfate could be corrected by the use of one and two-tenths pounds of precipitated carbonate. An equivalent amount of nitrogen in the form of ammonium phosphate, leunasalt peter, urea, and ammonium nitrate required 1.0, 0.9, 9.6, and 0.6 pounds of precipitated carbonate

respectively.

Allison (5) prepared a table showing the theoretical amount of calcium oxide required to neutralize the acidities formed from several nitrogenous fertilizers. From this table it appeared that mono-ammonium phosphate was capable of producing two or three times as much acidity as ammonium sulfate per unit of nitrogen. Allison pointed out, however, that because of the weak ionization of phosphoric acid, when ammonia was added to a weak solution of it, the first hydrogen was neutralized at about pH 4.4, the second at 7.8, and the third at 9.4. Under normal conditions, then, only one-third of the maximum acidity of the mono-ammonium phosphate would ordinarily be realized in the soil. He remarked that this agreed largely with Pierre's (58) results.

Ichikawa (56) found that additions of disodium phosphate and dipotassium phosphate made the soil slightly acid. The acidity was increased markedly with additions of dibasic ammonium phosphate.

## EXPERIMENTAL

### Purpose

The primary aim of this work was to determine the effect of phosphate fertilizers on soil reaction. To this end studies were made in Experiment 1 on Carrington silt loam comparing the effects of rock phosphate and superphosphate on reaction. Likewise, in Experiment 2 a series of pots of Grundy silt loam were treated in the greenhouse with different amounts of rock phosphate and sodium phosphate with and without lime for comparisons between the effects of these materials and the effect of lime. Having found in these tests that the phosphate fertilizers used had a significant effect on soil reaction, the scope of the work was broadened in Experiment 3 to determine the effects of five different phosphate carriers on the reaction of three different acid soils. The soils used in this experiment were Grundy silt loam from southern Iowa, Tama silt loam from eastern Iowa and Carrington silt loam from northeastern Iowa. They were selected as being representative of the large areas of acid soils in those sections of the state. Because of the recent interest in the more concentrated phosphates, especially the ammoniated phosphates, rock phosphate, superphosphate, Ammo Phos "A", ammoniated phosphate and treble superphosphate were used.

Experiment 2 was particularly designed for two purposes, namely, 1, to measure the effect of rock phosphate on soil reaction, and 2, to determine whether or not rock phosphate could be substituted for lime to supply calcium for plant nutrition.

More emphasis was placed on rock phosphate than on other forms of phosphate fertilizers because of the use of the term "lime phosphate" (34) in the fertilizer trade by a commercial company marketing a finely ground rock phosphate fertilizer and because of recommendations that rock phosphate be used as a filler in mixed fertilizers (71).

The attempt to isolate any effects that the calcium supplied by the rock phosphate might have other than its neutralizing effect was investigated because of the importance placed by many (2) (3) (4) (94) (64) (65) (10) on the nutritive value of calcium in limestone. If some of the benefit from liming is due to the calcium supplied regardless of the pH, it is possible that rock phosphate may be substituted for lime to supply calcium to the plant. In order to obtain some information on this point sodium phosphate was substituted for rock phosphate in Experiment 2 on the Grundy silt loam.

## Methods of Procedure

### 1. pH

The pH measurements were made with the quinhydrone electrode according to the recommendations of Billman and Jensen (12).

### 2. Lime Requirement

The soils were tested for lime requirement by the potassium thiocyanate method (31) and by the Truog lead acetate method (81). In Experiment 2 the lime requirement of the soil sampled at nine different dates was measured by the Hardy-Lewis method (29).

### 3. Exchangeable calcium

When the experiment was first started in 1930 the Schollenberger ammonium acetate method was used in the base exchange studies (68). However, the sum of the exchangeable hydrogen and exchangeable calcium in the limed soils was found to be greater than the base exchange capacity of the soil by this method. These results are in accord with those reported by Killinger (44), Dean (22), Dean (23), and Markle (51). Schollenberger and Dreibelbis (67) reported that one should expect the sum of replaceable bases and hydrogen to be greater than the base exchange capacity because of the presence of easily soluble cations other than those in the base exchange complex in soils. However, it seemed desirable to use some method of measurement which would avoid these apparent solubility effects. The alcoholic potassium chloride method of Chapman and Kelley (20)



was selected because it gave results which seemed to be more truly representative of actual exchangeable calcium than other methods tried.

#### 4. Exchangeable Hydrogen

The ammonium acetate method of Schollenberger and Dreiselbis (68) was used for determining exchangeable hydrogen in experiments 1 and 2.

#### 5. Base Exchange Capacity

A modification of the procedure recommended by Schollenberger and Dreiselbis (68) was followed in the determination of base exchange capacity. An open system so arranged as to keep the soil covered with the solution and to provide a continuous flow was developed and found to give comparable results with the closed system. The base exchange capacity was found to be practically the same with Parker's method as with the Schollenberger method.

#### 6. Other analyses

Available phosphorus was determined by the 0.002 N. sulfuric acid method of Truog (84). Harper's (30) modification of the phenoldisulfonic acid method was used to determine nitrates. The recommendations of the Association of Official Agricultural Chemists (7) were followed in determining the calcium content of the sweet clover, the magnesium nitrate method for total soil phosphorus and the Gunning-Hibbard method for total nitrogen.

## Results

### 1. The Effect of Rock Phosphate, 20 Per Cent Superphosphate and Lime Upon the Reaction of Carrington Loam.

The surface soil from a virgin area of Carrington loam having a pH of 6.0 and a lime requirement of 2 tons per acre was brought to the greenhouse, screened through a 1/4-inch sieve, mixed thoroughly and placed in 4-gallon pots. The soils were treated according to the outline given in table 1. The moisture content of the soil was adjusted to 50 per cent of the saturation capacity and maintained at that amount throughout the experiment by the addition of distilled water. Samples were taken at intervals for a determination of pH, and base exchange properties. The results obtained are presented in tables 2, 5 and 6.

The phosphates used were representative samples taken from sacks of the material as sold for commercial use. The analysis of the limestone showed it to contain the following:

Insol. material and Si.....	4.26%
Fe and Al oxides and Mn.....	3.81%
Calcium.....	23.01%
Magnesium.....	26.74%
Moisture content.....	1.64%
*Alkalinity test.....	98.50%

\*Sample boiled in hydrochloric acid and back titrated with sodium hydroxide.

#### Screen Test

Particles on 10-mesh screen.....	17.18%
" " 20-mesh "	22.39%
" " 40-mesh "	17.35%
" " 100-mesh "	28.82%

Table 1  
Outline of Treatments

Pot No.	Treatment
1. A and B	No treatment
2. A and B	1000 lbs. 300-mesh Ruhm's rock phosphate per acre
3. A and B	2000 lbs. 300-mesh Ruhm's rock phosphate per acre
4. A and B	120 lbs. 20% superphosphate per acre
5. A and B	240 lbs. 20% superphosphate per acre
6. A and B	4000 lbs. ground limestone per acre

a. pH

The effect of rock phosphate, superphosphate and lime on the reaction of Carrington loam as measured by pH of the original and treated soils at ten dates after the soils were treated is given in table 2.

An analysis of variance of the data was made, but because so much of the variation was due to the lime the analysis was again made, omitting the results obtained on the limed soils (table 3). The analysis then showed that the standard error of the difference between any pair of treatment means was

$$\sqrt{\frac{2(40.1)}{20}} = 2.0025$$

and the decoded value for sM was 0.020025. Corresponding to Fisher's 5 per cent point for 50 degrees of freedom, the value of  $t = 2.678$ . Therefore, the least mean difference which can be considered highly significant is  $2.678 \times .020025 = 0.0536$  pH.

The mean pH for the different treatments were as follows:

1. Check.....	5.787 pH
2. 1000 lbs. rock phosphate.....	5.854 pH
3. 2000 lbs. rock phosphate.....	5.890 pH
4. 120 lbs. 20% superphosphate.....	5.731 pH
5. 240 lbs. 20% superphosphate.....	5.67 pH
6. 4000 lbs. ground limestone.....	7.002 pH

The data show that both the 1000 lbs. and the 2000 lbs. of rock phosphate per acre increased the pH of Carrington loam in the greenhouse by a highly significant amount. The pH of the soil receiving 2000 lb. per acre of rock phosphate was significant greater than the pH of the soil receiving 1000 pound per acre of rock phosphate. The application of superphosphate decreased the

Table 2

The pH of Carrington Silt Loam Treated with Rock Phosphate,  
Superphosphate and Lime

Treatment			D A T E										
			1930				1931						
			11-21	12-13	12-20	12-27	1-3	1-10	1-17	2-14	3-14	4-11	6-15
Check	1.	A1	5.80	6.09	5.95	5.85	5.59	6.00	5.86	5.71	5.68	5.40	5.43
		A2	5.80	6.15	5.96	5.90	5.63	6.03	5.82	5.73	5.74	5.65	5.42
		B1	5.88	5.89	5.98	5.90	5.69	6.00	5.73	5.73	5.77	5.53	5.40
		B2	6.00	6.00	5.94	5.93	5.69	5.99	5.84	5.78	5.71	5.52	5.47
1000 lbs. rock phosphate	2.	A1	5.94	6.09	5.97	6.00	5.96	5.99	5.78	5.89	5.78	5.67	5.47
		A2	5.89	6.06	5.94	5.96	5.90	6.01	5.82	5.84	5.78	5.68	5.47
		B1	6.03	6.00	5.99	5.98	5.90	6.01	5.89	5.85	5.81	5.27	5.52
		B2	6.00	6.12	5.94	6.00	5.96	5.99	5.95	5.85	5.80	5.72	5.55
2000 lbs. rock phosphate	3.	A1	5.94	6.06	6.13	5.96	5.82	6.01	5.95	5.74	5.88	5.75	5.43
		A2	5.95	6.06	6.07	5.98	5.82	6.01	5.91	5.74	5.88	5.75	5.43
		B1	6.06	6.05	6.03	5.96	5.90	5.96	5.95	5.87	5.83	5.83	5.61
		B2	5.99	6.05	6.07	6.04	5.84	5.96	5.95	5.86	5.89	5.83	5.61
120 lbs. super-phosphate	4.	A1	5.91	5.85	5.66	5.83	5.73	5.82	5.78	5.75	5.71	5.63	5.52
		A2	5.85	5.85	5.67	5.83	5.80	5.90	5.76	5.73	5.67	5.63	5.53
		B1	6.01	5.70	5.67	5.83	5.69	5.89	5.73	5.77	5.75	5.70	5.56
		B2	6.06	5.76	5.76	5.76	5.69	5.89	5.83	5.75	5.68	5.67	5.53
240 lbs. super-phosphate	5.	A1	5.91	5.75	5.74	5.77	5.63	5.84	5.80	5.62	5.68	5.58	5.36
		A2	5.84	5.75	5.84	5.76	5.66	5.83	5.76	5.65	5.68	5.58	5.36
		B1	6.03	5.68	5.86	5.76	5.63	5.80	5.71	5.58	5.61	5.60	5.35
		B2	6.01	5.75	5.65	5.79	5.63	5.80	5.73	5.60	5.68	5.57	5.35
4000 lbs. ground limestone	6.	A1	5.85	6.84	7.07	6.90	6.87	7.09	7.08	7.23	7.26	7.23	7.10
		A2	5.92	6.84	7.07	6.93	6.87	7.07	7.08	7.30	7.32	7.21	7.12
		B1	6.10	6.77	6.93	6.95	6.89	7.11	7.07	7.20	7.19	7.17	7.05
		B2	6.04	6.71	6.92	6.93	6.90	7.12	7.12	7.20	7.20	7.17	7.05

Ave. pH of soil before treatment 5.93

Table 3

Analysis of Variance of the pli of Carrington  
Loam Treated with Rock Phosphate, Superphosphate and Lime

Source of Variation	D.f.	Total Sum of Squares	Mean Square
Total	199	6.31386	
Within	100	.24670	.00247 **
Between means of dates	9	3.94755	.43862 **
Between means of treatment	4	1.25720	.31430 **
Interaction	36	.66191	.01839 **
Experimental error		.20050	.00401

\*\* Mean square highly significant

$$s_{M_D} = \sqrt{2 \left( \frac{.00401}{20} \right)} = .020025$$

$$\frac{\bar{X}}{.020025} = 2.626$$

$M_D = .0525$  = least mean difference highly significant

pH of the Carrington loam by a highly significant amount. The pH of the soil receiving the 240 pound application was significantly lower than the pH of the soil receiving the 120 pound application.

When the analysis of variance was made on all of the data, including the results for the limed soil, the least mean difference which could be considered highly significant was 0.0448 pH, which is a little lower than the value found when the lime data were omitted from the analysis. When this figure, 0.0448 pH, is used for the comparison of mean differences essentially the same relationships are obtained as were obtained with the value 0.0525 pH, except that the 2000 pounds per acre application of rock phosphate produced an increase in pH of the soil highly significantly greater than the 1000 pound per acre application or that of the untreated soil. The application of lime to Carrington loam at the rate of 4000 pounds per acre produced an increase in pH of the soil over that of the other treatments by an amount which is much larger than the least mean difference considered highly significant.

These results show that rock phosphate in ordinary rates of application decreased the acidity of Carrington loam, whereas, superphosphate in ordinary rates of application increased the acidity. The high neutralizing value of lime was demonstrated. Whether these increases and decreases in acidity resulting from phosphate fertilizers are of magnitudes which would make much difference in the growth of "lime-loving" plants such as alfalfa and sweet clover remains a question that can be answered only by

actual field trials. Whether these differences are important from the practical standpoint and whether rock phosphate can be used to supply calcium in ordinary agricultural practices are questions that have not been answered. The possibilities suggested by these results should be checked by further experimentation.

## b. Base Exchange Properties

### (1) Preliminary studies on methods

Since Gedroiz's early work (27) many base exchange studies have been made and several new methods have been employed, but no one of these methods has been generally accepted as entirely satisfactory. Difficulty is usually encountered when one tries to duplicate the results obtained on a given soil by two methods. Bradfield (13) noted that the results obtained on the same soil by different methods were usually of the same order of magnitude but differed from each other considerably more than the experimental error with a single method.

Some of the uncertainty in regard to methods may be attributed to the lack of agreement among different workers concerning the nature of the base exchange complex and the manner in which the bases are held as Metzger (52) pointed out. The view that bases are held in chemical combination with replacement occurring according to well-defined chemical laws is generally supported by the work of Kelley and Brown (41), Burgess and McGeorge (19) and Kerr (43). Opposing this view is the theory proposed by Hissink (33) and apparently supported by Breazeale and Magistad



(14) and Oden (54) that the exchangeable cations are absorbed as an external layer around the colloid particle.

Chapman and Kelley (20) claim that the determination of replaceable bases is not an exact process and Kelley (40) would arbitrarily limit the term "base exchange" since it can not be correctly applied with precision to every reaction wherein the base of a solid becomes substituted by the base of a solution. This view was taken by Slater (74) who reported that the method to be used must be selected with regard to the particular study. If this is true the results of any base exchange study should be considered as specific only for the method used.

Aqueous solutions of salts such as KCl, NaCl, BaCl<sub>2</sub>, NH<sub>4</sub>Cl and NH<sub>4</sub>Ac have been tried by different workers but all have some dissolving effect on bases in soil carbonates and unweathered soil mineral particles. The same criticism is made of dilute HCl and of CH<sub>3</sub>COOH solutions. However, good results have been obtained by Magistad and Burgess (49) with an alcoholic solution of BaCl<sub>2</sub> and by Chapman and Kelley (20) with an alcoholic solution of KCl.

The results of some preliminary work by this method and the ammonium acetate method are presented in table 4.

The amounts of exchangeable calcium found in the unlimed soils by the alcoholic potash method were not much different from the amounts found by the ammonium acetate method, but the amounts found in the limed soils were much lower by the alcoholic potash method. The differences in the amount of exchangeable

Table 4

A Comparison of Methods for Determining the Exchange Calcium in Grundy Silt Loam

Treatment	M.E. Exch. Ca. per 100 gms. Dry Soil	
	: Alc.-KCl Method :	NH <sub>4</sub> Ac Method
No treatment	13.19	12.51
500# rock		
phosphate	13.99	12.71
1000# rock		
phosphate	13.00	12.82
1500# rock		
phosphate	12.45	14.68
2000# rock		
phosphate	13.99	15.04
2500# rock		
phosphate	14.09	14.94
3000# rock		
phosphate	14.09	14.33
1000# rock phosphate + 4 T. lime	18.46	23.36
2000# rock phosphate + 4 T. lime	18.64	23.05
Na <sub>3</sub> PO <sub>4</sub> equiv. 1000# rock phosphate	13.42	14.84
Na <sub>3</sub> PO <sub>4</sub> equiv. 2000# rock phosphate	13.68	14.99
Na <sub>3</sub> PO <sub>4</sub> equiv. 1000# rock phosphate + 4 tons lime	18.67	22.67
Na <sub>3</sub> PO <sub>4</sub> equiv. 2000# rock phosphate + 4 tons lime	17.33	23.05
4 tons lime	18.91	23.15

calcium found in limed soils and that found in unlimed soils was not so marked when the alcoholic KCl method was used as when the  $\text{NH}_4\text{AOC}$  method was used. This indicates that less soluble calcium from the  $\text{CaCO}_3$  was appearing in the leachate of the alcoholic KCl. However, the sum of exchangeable calcium and hydrogen in the limed soil was greater than the exchange capacity, even when the exchangeable calcium was determined by the alcoholic-KCl method.

It was thought that the sum of the exchange Ca and H might be too high because of the H as well as the Ca. Since the sum of the exchangeable calcium and exchangeable hydrogen in the limed soils was greater than the base exchange capacity, even when the alcoholic-KCl method was used, the possibility that the amount of exchangeable hydrogen was too large was investigated.

Hence, a preliminary study to compare Parker's (55) barium acetate method, the ammonium acetate method with a closed system and the ammonium acetate method with an open system was made.

The ammonium acetate and barium acetate methods for measuring replaceable hydrogen were found to give comparable results but better agreement between duplicates was secured with the barium acetate than with the ammonium acetate method. No appreciable difference was found between the results obtained with the open and the closed system of leaching by the ammonium acetate method.

Walker (91) reported higher exchangeable hydrogen by the barium acetate method than by the ammonium acetate method.

Markle (51) considered the results obtained with the ammonium acetate method too low.

The base exchange capacity of most soils is regarded as a fairly well fixed quantity according to Walker and Brown (92). Dean (22) found no change in base exchange capacity of the soil following additions of different amounts of calcium and magnesium limestones. Robinson (64) even suggested the use of the absorbing complex as a basis for soil characterization because of its constancy over a period of years. On the other hand, Markle (51) found that different management practices changed the base exchange capacity of the soils of the Pennsylvania plots and Tiulin and Bystrova (79) claimed a permanent increase in the exchange capacity of soils treated with alkalis. That strong alkali tends to build up the base exchange capacity of the soil was also borne out by the work of Burgess (18) and Schollenberger and Dreibelbis (68). The effect of phosphates on the exchange capacity of the soil was also determined.

Preliminary studies were made on methods for determining base exchange capacity of the soil and it was noted that variations in the amount of ammonia used to neutralize the alcohol employed in leaching the excess ammonia from the soil produced very marked differences. This was especially troublesome because of the indefinite end point with bromo-thymol blue, the indicator recommended by Schollenberger and Dreibelbis (68).

A statistical analysis of the data showed no significant difference between the base exchange capacity of any of the soils

due to the different treatments of phosphates.

These data seemed to justify the use of the mean base exchange capacity for calculating the replaceable bases and the degree of saturation. Whether these differences are important from the practical standpoint and whether rock phosphate can be used to supply calcium in ordinary agricultural practices are questions that have not been answered. The possibilities suggested by these results should be checked by further experimentation.

## (2) Major studies

The amount of replaceable hydrogen in the soils at two different dates and the mean replaceable hydrogen of the differently treated soils are given in table 5.

The mean exchangeable hydrogen of the soils receiving the 1000- and the 2000-pound per acre applications of rock phosphate was about the same and at least 0.4 M.E. lower than the average amount of exchangeable hydrogen in the untreated soil. The applications of superphosphate increased the average amount of replaceable hydrogen over that of the check soil. The application of lime decreased the average exchangeable hydrogen in the soil practically one-third of the total.

The data show that both rock phosphate and ground limestone decreased the acidity of Carrington loam as measured by the content of exchangeable hydrogen.

A correlation between the average pH of the variously treated

Table 5

Replaceable Hydrogen, Base Exchange Capacity, Content of

Treatment	Untreated soil					
	November 21, 1950					
	Exchange:	Exchange:	Exchange:	Degree	Exchange	
	hydrogen:	capacity:	bases	of	hydrogen	
	M.E.	M.E.	M.E.	saturation:	M.E.	
	:	:	:	%	:	
1. A Check	3.0	13.66	15.66	83.9	6.0	
B					6.0	
2. A 1000 lbs.	4.0		14.66	78.5	5.15	
B Rock phosphate					5.0	
3. A 2000 lbs.	6.9		11.76	63.0	4.5	
B Rock phosphate					4.4	
4. A 120 lbs.	4.0		14.66	78.5	6.5	
B Superphosphate					6.5	
5. A 240 lbs.					5.3	
B Superphosphate					5.5	
6. A 4000 lbs.					2.3	
B Ground limestone					2.6	
Ave.	4.47		14.19	76.0		

Note: The values of base exchange capacity, exchangeable hydrogen, milligrams per hundred grams of soil.

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# Replaceable Bases, and Degree of Saturation of Carrington Loam

April 11, 1931				June 13, 1931				Treatment
Exchange capacity:	Exchange bases:	Degree of saturation:	of	Exchange capacity:	Exchange bases:	Degree of saturation:	of	Means for Exchange
M.E.	M.E.	%		M.E.	M.E.	M.E.	%	hydrogen M.E.
18.66	12.66	67.8	7.61	18.66	11.05	59.2	6.80	
	12.66	67.8	7.72		10.94	58.6	6.86	
	13.51	72.4	7.72		10.94	58.6	6.44	
	13.66	73.2	7.72		10.94	58.6	6.36	
	14.16	75.8	8.40		10.26	54.9	6.45	
	14.26	76.4	8.40		10.26	54.9	6.40	
	12.16	65.1	8.40		10.26	54.9	7.45	
	12.16	65.1	8.40		10.26	54.9	7.45	
	13.36	71.5	8.81		9.85	52.7	7.06	
	13.16	70.5	9.02		9.64	51.6	7.26	
	16.36	87.6	6.07		12.59	67.4	4.18	
	16.06	86.1	6.49		12.17	65.2	4.54	

Hydrogen and exchangeable bases are expressed in terms of





soils at 10 different samplings and the average content of exchangeable hydrogen measured at two dates gave a correlation coefficient of  $-0.9644$ , a highly significant amount. Earlier in this paper it was pointed out that in the experiment both rock phosphate and ground limestone were found to increase the pH by a highly significant amount while superphosphate decreased the pH by a highly significant amount.

The base exchange capacity of the variously treated soils (table 6) varied at different dates but a statistical analysis of the data (table 7) showed that the differences were not significant.

The data in table 5 show further that the applications of rock phosphate increased the amount of replaceable bases and the degree of saturation in the different soils proportionately as it decreased the amount of replaceable hydrogen. On the other hand, the applications of superphosphate decreased the content of replaceable bases and the degree of saturation.

The content of replaceable bases was assumed to be the difference between the exchange capacity and the content of replaceable hydrogen. Naturally, then, since the same value for exchange capacity was used throughout, the amount of replaceable bases varied inversely as the content of exchangeable hydrogen. The same relationships between treatment and the content of exchangeable hydrogen held between treatment and the content of exchangeable bases. The same is true of the degree of saturation since this value was obtained by the formula

Table 6  
Base Exchange Capacity of Carrington Loam

Treatment	M.E. per 100 gm. soil	
	Nov. 21, 1933	June 13, 1934
1 A Check	19.50	: 17.91
B	18.62	17.50
2 A 1000# rock	17.98	: 17.64
B phosphate	18.78	17.40
3 A 2000# rock	19.05	: 18.33
B phosphate	20.68	18.22
4 A 120# 20%	18.30	: 17.62
B superphosphate	18.51	: 19.94
5 A 240# 20%	19.23	: 18.98
B superphosphate	19.89	19.54
6 A 4000# ground	18.42	: 18.57
B limestone	18.29	19.14

Table 7  
Analysis of Variance of Base Exchange Capacity  
of Carrington Loam

Source of variation	Degrees of freedom	Sum of squares	Mean square
Total	23	16.2731	1.7388
Between means of dates	1	1.7388	1.7388
Between means of treatment	5	5.2755	1.0551
Interaction	5	3.8455	0.7691
Within	12	5.4133	0.4511

For these small degrees of freedom the least mean square which would be highly significant is 4.75.

$$100 \times \frac{\text{replaceable bases in M.E.}}{\text{Exch. capacity in M.E.}} = \text{degree of saturation.}$$

The data show that the acidity of all soils increased with time. The content of exchangeable hydrogen in the check soil was twice as high five months after treatment as it was in the same soil when the experiment was started. Likewise, all soils contained a higher content of exchangeable hydrogen seven months after treatment than five months after treatment.

## 2. The Effect of Rock Phosphate and Sodium Phosphate With and Without Lime and Lime Alone on the Grundy Silt Loam

The effects of different amounts of rock phosphate and of sodium phosphate in comparison with limestone on the reaction of Grundy silt loam was studied in this experiment. Grundy silt loam, having a lime requirement of approximately 3 -1/2 tons per acre and a pH of 5.30 was brought to the greenhouse, sieved through a 1/4-inch screen and 30 pounds of dry soil placed in each of 56 4-gallon pots.

The average phosphorus content of this original soil was 0.08 per cent and the average nitrogen content was 0.23 per cent.

The soils were treated according to the following plan:

1. Check
2. 500 lbs. Ruhm's 300-mesh rock phosphate per acre\*
3. 1000 lbs.   "           "           "           "           "           "

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\*The treatments were made on the basis of 2,000,000 pounds per acre of surface soil and the fertilizer was thoroughly mixed with the soil.

4. 1500 lbs. Ruhm's 300-mesh rock phosphate per acre
5. 2000 lbs.     "             "             "             "             "
6. 2500 lbs.     "             "             "             "             "
7. 3000 lbs.     "             "             "             "             "
8. 1000 lbs. Ruhm's 300-mesh rock phosphate per acre + 4 T.  
limestone per acre
9. 2000 lbs. Ruhm's 300-mesh rock phosphate per acre + 4 T.  
limestone per acre
10. 1278 lbs. sodium phosphate, equivalent to 1000 lbs. rock  
phosphate per acre
11. 2557 lbs. sodium phosphate, equivalent to 2000 lbs. rock  
phosphate per acre
12. 1278 lbs.  $\text{Na}_3\text{PO}_4$  + 4 T. of limestone per acre
13. 2557 lbs.  $\text{Na}_3\text{PO}_4$  + 4 T. limestone per acre
14. 4 T. ground limestone per acre

The moisture content of the soils was adjusted to 50 per cent of the saturation capacity and maintained at that amount by additions of distilled water. Of the four pots per treatment, two were fallowed and used for sampling and two were seeded to sweet clover. A sub-irrigation system was used in watering the cropped pots.

The rock phosphate was taken from a sack of commercial material having the following guaranteed analysis:

"Effectual" $\text{P}_2\text{O}_5$	30.15 per cent
Calcium	33.0 per cent
Passing a 300-mesh screen	80.0 per cent

Upon analysis a sample of the rock phosphate used in the experiment was found to contain 30.27 per cent  $\text{P}_2\text{O}_5$ . C.p.  $\text{CaCO}_3$  and

$\text{Na}_2\text{PO}_4$  were used. The fallow soils were sampled at intervals for a determination of pH, exchangeable hydrogen and base exchange capacity, exchangeable calcium, available phosphate, nitrate nitrogen, and lime requirement. The results obtained are presented in tables, 8, 12, 15, 17, and 21.

a. pH

The pH of the soils determined over a period of 20 months is given in table 8. To simplify the interpretation of the results and to secure the variability for rock phosphate treatments alone, the data were divided into two parts for the statistical analysis after first making an analysis of variance on the complete data in table 8.

The first set consisted of the data of the entire 14 treatments, whereas, the second set consisted only of the data for the first seven pairs of pots, or the check and the rock phosphate treatments only.

An analysis of variance of the combined data of tables 8 and 9 showed that for the 14 treatments the variation due to time and the variation due to treatment were each highly significant.

The experimental error between the pH of soils of the same treatment on each data was found to be 0.001 pH. This variance was used in calculating the significance of the differences between the treatment means for the entire 14 pairs of pots.

In part B of table 9 the analysis of variance was made on the data from the soils receiving different amounts of rock phosphate. The mean squares were smaller than where the results

Table 8

The Effect of Rock Phosphate and Sodium Phosphate Alone and with  
of Grundy Silt Lo

Treatment	1933						pH
	1-11	2-18	3-11	4-11	5-19	7-11	
1 A Check	5.24	5.18	5.28	5.04	5.04	5.03	
B	5.24	5.18	5.28	5.10	5.04	5.03	
2 A 500# rock phosphate	5.32	5.23	5.36	5.09	5.17	5.01	
B	5.27	5.23	5.33	5.10	5.17	5.03	
3 A 1000# rock phosphate	5.29	5.23	5.31	5.12	5.14	5.06	
B	5.32	5.23	5.28	5.15	5.14	5.06	
4 A 1500# rock phosphate	5.34	5.18	5.28	5.15	5.11	5.03	
B	5.34	5.18	5.28	5.15	5.14	5.02	
5 A 2000# rock phosphate	5.34	5.20	5.28	5.12	5.14	5.06	
B	5.32	5.23	5.24	5.09	5.14	5.05	
6 A 2500# rock phosphate	5.34	5.22	5.28	5.12	5.24	5.15	
B	5.34	5.24	5.24	5.15	5.24	5.13	
7 A 3000# rock phosphate	5.31	5.10	5.36	5.15	5.18	5.08	
B	5.34	5.14	5.38	5.17	5.18	5.08	
8 A 1000# rock phos. + 4 T. lime	7.36	7.13	7.12	6.82	6.75	6.62	
B	7.38	7.08	7.09	6.80	6.75	6.62	
9 A 2000# rock phos. + 4 T. lime	7.46	7.09	7.18	6.95	6.78	6.69	
B	7.49	7.11	7.19	6.92	6.75	6.65	
10 A $\text{Na}_3\text{PO}_4$ = 1000# rock phos.	5.60	5.48	5.56	5.59	5.27	5.15	
B	5.65	5.48	5.59	5.59	5.31	5.16	
11 A $\text{Na}_3\text{PO}_4$ = 2000# rock phos.	5.93	5.85	6.02	5.61	5.54	5.41	
B	5.92	5.84	6.04	5.66	5.54	5.38	
12 A $\text{Na}_3\text{PO}_4$ = 1000# rock phos. + 4 T. lime	7.64	7.39	7.46	7.02	7.03	6.77	
B	7.65	7.41	7.49	7.04	7.06	6.75	
13 A $\text{Na}_3\text{PO}_4$ = 2000# rock phos. + 4 T. lime	7.71	7.44	7.66	7.12	7.21	6.91	
B	7.71	7.44	7.66	7.12	7.21	6.93	
14 A 4 T. lime	7.50	7.24	7.22	7.02	6.91	6.62	
B	7.47	7.26	7.18	7.02	6.93	6.62	

Average pH of soil before treatment was 5.31





Table 8

ate Alone and with Lime and of Lime Alone on the pH  
Grundy Silt Loam

pH									Treatment Means
5-19	7-11	8-14	9-14	11-23	1-13	3-10	4-11	8-11	
5.04	5.03	4.98	4.73	4.99	5.03	5.00	4.69	4.93	
5.04	5.03	5.01	4.84	4.99	5.06	5.00	4.71	5.00	5.02
5.17	5.01	5.01	4.85	5.02	4.98	5.11	4.69	4.93	
5.17	5.03	4.98	4.88	5.02	5.00	5.11	4.69	4.96	5.06
5.14	5.06	4.98	4.85	5.02	5.03	5.09	4.66	4.95	
5.14	5.06	5.01	4.83	5.02	5.01	5.09	4.69	4.90	5.06
5.11	5.03	4.98	4.81	4.97	5.01	5.06	4.61	4.91	
5.14	5.02	5.01	4.90	4.97	5.01	5.07	4.66	5.27	5.06
5.14	5.06	5.01	4.88	5.06	5.05	5.07	4.68	5.00	
5.14	5.05	4.98	4.89	5.07	5.08	5.11	4.71	4.96	5.07
5.24	5.15	4.94	4.88	5.04	5.08	5.02	4.69	4.90	
5.24	5.13	4.96	4.95	5.06	5.15	5.08	4.75	4.98	5.08
5.18	5.08	4.98	4.95	5.09	5.02	5.03	4.71	4.93	
5.18	5.08	4.98	4.98	4.99	5.02	5.07	4.71	4.86	5.07
6.75	6.62	6.59	6.45	6.45	6.55	6.51	5.47	6.42	
6.75	6.62	6.55	6.44	6.47	6.55	6.51	5.50	6.33	6.63
6.78	6.69	6.72	6.60	6.57	6.55	6.51	5.60	6.43	
6.75	6.65	6.66	6.60	6.60	6.62	6.51	5.60	6.37	6.70
5.27	5.15	5.15	5.11	5.14	5.09	5.17	5.05	5.13	
5.31	5.16	5.15	5.19	5.14	5.07	5.17	5.07	5.20	5.28
5.54	5.41	5.38	5.30	5.30	5.31	5.32	5.01	5.23	
5.54	5.38	5.38	5.32	5.35	5.34	5.32	4.95	5.23	5.48
7.03	6.77	6.75	6.59	6.62	6.69	6.68	5.58	6.53	
7.08	6.75	6.75	6.56	6.61	6.69	6.67	5.47	6.53	6.82
7.21	6.91	6.82	6.69	6.79	6.73	6.69	6.08	6.60	
7.21	6.93	6.82	6.63	6.81	6.78	6.71	5.88	6.53	6.95
6.91	6.62	6.61	6.59	6.61	6.60	6.50	5.83	6.30	
6.93	6.62	6.60	6.54	6.54	6.60	6.50	5.70	6.30	6.72

5.31



Table 9

Analysis of Variance of pH Values of Grundy Silt Loam Treated with Different Amounts of Rock Phosphate and Sodium Phosphate With and Without Lime and with Lime Alone

Source of Variation	: Degrees of freedom	: Sum of Square	: Mean square
(a)			
Total	363	265.1973	.7306
Within date--treatment groups	182	.1907	.001
Between means of dates	12	26.99	2.25 **
Between means of treatments	13	229.67	17.67 **
Interaction	156	8.35	.05

(b)

Analysis of Variance of pH Values of Grundy Silt Loam Treated with Different Amounts of Rock Phosphate (Same data as above but omitting the results for the soils treated with sodium phosphate and with lime)

Total

Within date--treatment groups

Between means of dates	12	474.27	39.52 **
Between means of treatments	6	5.38	.90 *
Interaction	72	24.03	.33

\*\* Means highly significant

\* Means significant

of  $\text{Na}_3\text{PO}_4$  and lime were included in the analysis. Where the data from the check and the rock phosphate treated soils alone were considered the variation due to treatment was 0.90 and where all 14 treatments were used in the analysis, the value was 17.67.

According to the test of significance the value 0.90 represents a significant difference due to rock phosphate alone but a highly significant difference was not found when the variability due to all 14 treatments was considered. This shows that although rock phosphate corrected some soil acidity, it was not as effective as  $\text{Na}_3\text{PO}_4$  or lime.

The analysis of variance of the data shows the very low experimental error and the very high significance of the difference due to treatment. The least highly significant mean difference was found to be 0.023 pH.

Checking the treatment means of the first 7 treatments as given in table 10 with this figure shows that there was a highly significant increase in pH following the application of rock phosphate at the rate of from 500 to 3000 pounds per acre. However, after the first 500 pounds, increments of 500 pounds of rock phosphate per acre did not produce differences in pH which were significant except for the 2500 pound rate which brought about an increase in the pH that was highly significant when compared to the 500, 1000 and 1500 pound rates of application. Likewise, the 2000, 2500 and 3000 pound per acre applications of rock phosphate produced a higher pH of the soil than the 500, 1000 and 1500 pound applications. This indicates that 500 pounds

Table 10

Treatment Means of pH Values for Grundy Silt Loam  
Treated with Different Amounts of Rock Phosphate

Pot No.	Treatment	Treatment Means
1	Check	5.025
2	500# rock phosphate	5.059 *
3	1000# rock phosphate	5.056 *
4	1500# rock phosphate	5.055 *
5	2000# rock phosphate	5.068 *
6	2500# rock phosphate	5.083 **
7	3000# rock phosphate	5.073 *

Least highly significant mean difference = 0.023 pH

\* Very significantly higher than No. 1  
\*\* Very significantly higher than Nos. 1, 2, 3, 4

per acre or more rock phosphate increased the pH of the Grundy silt loam a highly significant amount and that there was a tendency for increased amounts of phosphate beyond the 500 pound application to increase the pH proportionately.

The arrangement of the treatment means of the pH determinations according to the order of magnitude in table 11 shows the relative effects of the different treatments on pH. Sodium phosphate with lime was more effective in neutralizing soil acidity than was lime alone, whereas, rock phosphate with lime did not decrease the acidity as much as did the lime alone. However, the 1000 pounds and 2000 pounds per acre applications of rock phosphate alone increased the pH over that of the untreated soil by a highly significant amount. The possibility that rock phosphate with lime produced a more favorable environment for bacterial activity than did sodium phosphate with lime may account for the increased acidity where the former combination was used. However, such an assumption can not be verified from the data at hand. Sodium phosphate equivalent to 1000 pounds per acre of rock phosphate was more effective in decreasing the acidity of the soil than 1000 pounds per acre of rock phosphate. Sodium phosphate equivalent to 2000 pounds per acre of rock phosphate was more effective in decreasing the acidity of the soil than 1000 pounds per acre of rock phosphate. Sodium phosphate equivalent to 2000 pounds per acre of rock phosphate was more effective in decreasing the acidity of the soil than that amount of rock phosphate and also more effective than the

Table 11

Treatment Means for pH Values of Grundy Silt Loam Treated with Different Amounts of Rock Phosphate and of Sodium Phosphate With and Without Lime and With Lime Alone Arranged in Order of Magnitude

Pot No.	:	Treatment	Treatment Means
13	:	2557# Sodium phosphate + lime	6.953
12	:	1278# Sodium phosphate + lime	6.823
14	:	Lime	6.723
9	:	2000# Rock phosphate + lime	6.700
8	:	1000# Rock phosphate + lime	6.627
11	:	2000# Sodium phosphate	5.480
10	:	1000# Sodium phosphate	5.277
5	:	2000# Rock phosphate	5.068
3	:	1000# Rock phosphate	5.056
1	:	Check	5.025

Least mean difference highly significant = 0.023 pH.



smaller application of sodium phosphate. Likewise, all the lime treatments were effective in controlling acidity but as noted above rock phosphate and lime produced a lower pH than did lime alone, whereas, each 1000 pound increment of  $\text{Na}_2\text{PO}_4$  per acre in combination with lime increased the pH. All these differences due to treatment and shown as treatment means were larger than the least mean difference which could be considered highly significant.

b. Lime Requirements

The averages of duplicate determinations of lime requirement on soils taken from the greenhouse at nine dates are given in table 12.

Lime and sodium phosphate decreased the lime requirement of Grundy silt loam and there was also an apparent tendency for rock phosphate to decrease the lime requirement of this soil but these differences were not very marked. An analysis of variance of the data was made to test the significance of these differences. The summary of this analysis is given in table 13.

Only that part of the data which concerned the check soil and the soil treated with various amounts of rock phosphate was analyzed in order to test the significance of the effect of the rock phosphate alone.

The data in table 13 show that the variance between treatments was highly significant. Although the analysis of variance shows the differences due to treatment to be highly significant,

Table 12

Influence of Different Amounts of Rock Phosphate and Sodium Phosphate Alone and in Combination with Lime and of Lime Alone on the Lime Requirement of Grundy Silt Loam in Pounds per Acre

Treatment	Date of Sampling									Treatment Mean
	1-11 :1933	2-18 :1933	3-11 :1933	4-11 :1933	5-19 :1933	7-11 :1933	7-11 :1933	8-14 :1933	3-10 :1934	
Check	6206	5280	6570	7884	6189	5931	5889	5995	5959	6211
500# rock phos.	6111	5071	6074	6945	6214	6042	5830	5913	5924	6014
1000# rock phos.	6111	4888	6104	6926	5796	6398	5749	5971	5960	5989
1500# rock phos.	6165	4630	6078	7663	5821	6828	5789	5889	6216	6119
2000# rock phos.	4142	4703	6115	6705	6214	6729	5667	5796	5971	5782
2500# rock phos.	6098	4396	4470	5784	5772	6361	5633	5936	6030	5608
3000# rock phos.	5989	4433	4630	5868	6018	6361	5655	5690	5901	5616
1000# rock phos. + 4 T. lime	910	884	1350	1548	2002	1596	1519	1028	1624	1384
2000# rock phos. + 4 T. lime	815	1253	1130	1597	1817	1818	1730	1531	1484	1463
Na <sub>3</sub> PO <sub>4</sub> = 1000# rock phos.	5018	4077	3684	4323	6079	6312	6006	5691	5726	5212
Na <sub>3</sub> PO <sub>4</sub> = 2000# rock phos.	4970	3905	4617	2997	6361	5465	5200	5399	5691	4955
Na <sub>3</sub> PO <sub>4</sub> = 1000# rock phos. + 4 T. lime	856	1130	1191	811	1400	1548	1473	1344	1391	1238
Na <sub>3</sub> PO <sub>4</sub> = 2000# rock phos. + 4 T. lime	978	1130	713	841	1424	1572	1496	1075	1321	1172
4 T. lime	964	848	762	958	1535	1609	1531	1192	1332	1192
Least mean difference highly significant = 90										

Table 13

Analysis of Variance of Lime Requirement of Grundy Silt Loam  
Treated with Different Amounts of Phosphate Fertilizers with  
and without Lime and Treated with Lime Alone

Source of Variation	Degrees of freedom (a)	Sum of squares	Mean square
Total	251	1,258,911,091	5,015,584 *
Within date--treatment groups	126	1,450,749	11,514 *
Between means of dates	8	33,932,390	4,241,549 *
Between means of treatments	13	1,163,997,898	89,538,300 *
Interaction	104	59,530,654	572,410 *
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(b)			
Analysis of the same data but with results of soils receiving lime or sodium phosphate omitted			
Between means of dates	8	34,140,566	4,267,571 *
Between means of treatments	6	6,212,110	1,035,352 *
Interaction	48	19,749,713	411,452 *

\* Highly significant.

there still remains the question of the significance of the decrease in acidity from any single pair of similarly treated soils to the next. In order to determine this, the lowest significant and highly significant values of the mean differences in lime requirement from any single treatment for all nine dates were calculated. For this comparison the lowest mean difference to be significant is 71 pounds of lime per acre and the lowest mean difference to be highly significant is 94 pounds per acre.

In table 14 the treatment means expressed as pounds of limestone per acre required to neutralize Grundy silt loam are given. Every rate of application of rock phosphate decreased the mean lime requirement below that of the check soil by a highly significant amount but every increment of 500 pounds in rate of application did not always cause a highly significant lowering of lime requirement.

The treatment means for the 500, 1000 and 1500 pound rates of application are all lower than that of the untreated soil by a highly significant amount but are not highly significantly different from each other. However, the treatment mean of the 2000-pound rate is significantly lower than any of those of the three above mentioned rates of application. Likewise, rates of 2500 and 3000 pounds per acre each lowered the mean lime requirement below that of the 2000 pound rate by a highly significant amount, although the difference between the two was not significant. These results show a definite trend toward lessened acidity with 500 pounds per acre increments of rock phosphate.

Table 14

Treatment Means for Lime Requirement Values for Grundy Silt Loam Treated with Different Amounts of Rock Phosphate and of Sodium Phosphate with and without Lime and with Lime Alone Arranged in Order of Magnitude

Pot : No. :	Treatment	: Treatment Means :Lbs. per acre lime : needed
13	2557# $\text{Na}_3\text{PO}_4$ + 4 T. lime	1172
14	4 T. lime	1192
12	1278# $\text{Na}_3\text{PO}_4$ + 4 T. lime	1238
8	1000# rock phosphate + 4 T. lime	1384
9	2000# rock phosphate + 4 T. lime	1463
11	2557# $\text{Na}_3\text{PO}_4$	4955
10	1278# $\text{Na}_3\text{PO}_4$	5212
5	2000# rock phosphate	5782
3	1000# rock phosphate	5989
1	Untreated	6211

Least mean difference highly significant = 90 lbs.

The effects of the different treatments on reaction as measured by lime requirements were, in general, the same as those measured by pH. In general,  $\text{Na}_3\text{PO}_4$  in the rates used reduced acidity more than rock phosphate in equivalent amounts. Lime alone or with phosphate quite markedly raised the pH of the Grundy silt loam.

Each rate of sodium phosphate when used in combination with lime was more effective than lime alone in controlling acidity as determined by pH, whereas the rock phosphate in combination with lime was less effective than lime alone. In table 15 it can be seen that in the lime requirement studies the higher rate of sodium phosphate with lime and lime alone could be considered as equally effective in controlling acidity, there being no significant difference between the effects of the two treatments. Lime in combination with the smaller amount of  $\text{Na}_3\text{PO}_4$  was not as effective as was lime alone in decreasing lime requirement, although still more effective than the applications of rock phosphate with lime.

As measured by pH 2000 pounds of rock phosphate with lime neutralized the acidity of the soil by a significantly higher amount than that produced by 1000 pounds of rock phosphate with lime. As measured by lime requirement, the 2000 pound application of rock phosphate with lime was still the most effective of all the treatments.

The lime requirement of all of the soils varied by a highly significant amount. Sodium phosphate at 2557 pounds per acre

was not as good a neutralizer of acidity as lime alone.  $\text{Na}_3\text{PO}_4$  at both rates of application was a better neutralizer of soil acidity than rock phosphate at either rate of application. Two thousand pounds of rock phosphate per acre were more effective than 1000 pounds per acre. The mean lime requirement of the soils treated with the rock phosphate was significantly lower than that of the untreated soil.

### c. Base Exchange Properties

Base exchange determinations were made on soils sampled at three different dates. The data obtained are presented in table 15.

A statistical analysis of the data on base exchange capacity showed no significant difference which could be attributed to treatment. Consequently, the average value for base exchange capacity was used in calculating total replaceable bases and degree of saturation.

Since the content of replaceable bases was figured as the difference between exchangeable hydrogen and base exchange capacity and the degree of saturation was calculated from the formula

$$\frac{\text{base exchange cap.} - \text{exch. H}}{\text{base exchange capacity}} \times 100 = \text{degree of saturation}$$

it appears that the content of exchangeable hydrogen was the most important variable in the base exchange studies.

The data in table 15 show the marked effect of lime in lowering the content of exchangeable hydrogen. Rock phosphate

Exchangeable Hydrogen Content and Total Exchange Capacity of Gr  
Amount of Exchangeable Bases and

Treatment	7-11-33 (7 months)				11-23	
	Exch. H. M.E.	Exch. capacity M.E.	Exch. bases M.E.	Degree of saturation %	Exch. H. M.E.	Exch. capacity M.E.
1 A Check	8.81	27.58	18.77	68.0	10.01	27.58
B	8.20		19.38	70.2	9.84	
2 A 500# rock phosphate	9.64		17.94	65.0	10.15	
B	9.64		17.94	65.0	10.25	
3 A 1000# rock phosphate	10.87		16.71	60.5	10.25	
B	10.25		17.33	62.8	10.25	
4 A 1500# rock phosphate	9.23		18.35	66.5	9.64	
B	9.23		18.35	66.5	-	
5 A 2000# rock phosphate	9.23		18.35	66.5	10.25	
B	8.61		18.97	68.8	8.20	
6 A 2500# rock phosphate	8.00		19.58	71.0	6.15	
B	7.79		19.79	71.7	6.97	
7 A 3000# rock phosphate	7.79		19.79	71.7	11.89	
B	7.38		20.20	73.2	12.71	
8 A 1000# rock phos. + 4 T.	1.23		26.35	95.5	8.81	
B lime	1.03		26.55	96.3	9.84	
9 A 2000# rock phos. + 4 T.	1.03		26.55	96.3	7.59	
B lime	2.46		25.12	91.1	10.25	
10 A $\text{Na}_3\text{PO}_4$ = 1000# rock phos.	7.18		20.40	74.0	12.51	
B	6.77		20.81	75.4	12.71	
11 A $\text{Na}_3\text{PO}_4$ = 2000# rock phos.	5.95		21.63	78.4	11.89	
B	5.13		22.45	81.4	12.71	
12 A $\text{Na}_3\text{PO}_4$ = 1000# rock phos.	0		27.58	100.0	3.08	
B + 4 T. lime	1.03		26.55	96.3	6.15	
13 A $\text{Na}_3\text{PO}_4$ = 2000# rock phos.	1.64		25.94	94.1	3.08	
B + 4 T. lime	0.82		26.76	97.0	2.87	
14 A 4 T. lime	1.64		25.94	94.0	2.87	
B	1.03		26.55	96.3	4.10	

Note: The values of base exchange capacity, exchangeable hydrogen and  
of milligrams per hundred grams of soil.





Table 15

Brandy Silt Loam by the Ammonium-Acetate Method and the Calculated  
and the Degree of Saturation

2-23-33 (11 months)				8-11-34 (20 months)				Treatment Means for Exchange Hydrogen M.E.
Exch. capa- city M.E.	Exch. bases M.E.	Degree of satur- ation %	Exch. H. M.E.	Exch. capa- city M.E.	Exch. bases M.E.	Degree of Satur- ation %		
27.58	17.57	63.7	10.25	27.58	17.33	62.8	9.56	
	17.74	64.3	10.25		17.33	62.8		
	17.43	63.2	10.25		17.33	62.8	10.10	
	17.33	62.8	10.66		16.92	61.3		
	17.33	62.8	12.92		14.66	53.2	11.38	
	17.33	62.8	13.74		13.84	50.2		
	17.94	65.0	12.92		14.66	53.2	10.60	
	-		12.92		14.66	53.2		
	17.33	62.8	13.74		13.84	50.2	10.59	
	19.38	70.3	13.53		14.05	50.9		
	21.43	77.7	14.35		13.23	48.0	9.60	
	20.61	74.7	14.35		13.23	48.0		
	15.69	56.9	14.76		12.82	46.4	11.55	
	14.87	53.9	14.76		12.82	46.4		
	18.77	68.1	4.10		23.48	85.1	5.23	
	17.74	64.3	6.36		21.22	76.9		
	19.99	72.5	6.77		20.81	75.4	5.81	
	17.33	62.8	-					
	15.07	54.6	10.87		16.71	60.5	10.32	
	14.87	53.9	11.89		15.69	56.9		
	15.69	56.9	-				8.68	
	14.87	53.9	8.20		19.38	70.3		
	24.50	88.8	2.87		24.71	89.6	2.67	
	21.43	77.7	2.87		24.71	89.6		
	24.50	88.8	1.44		26.14	94.8	2.05	
	24.71	89.6	2.46		25.12	91.1		
	24.71	89.1	2.05		25.53	92.6	2.53	
	23.48	85.1	3.49		24.09	87.3		

and exchangeable bases are expressed in terms



was not as effective as lime and sodium phosphate or as lime alone in neutralizing soil acidity.

As measured by pH both 1278 pounds and 2557 pounds of sodium phosphate per acre in addition to 4 tons of lime were more effective than lime alone but as measured by lime requirement only the 2557 pounds of sodium phosphate with lime was as effective as lime alone. The content of exchangeable hydrogen agrees with that of the lime requirement measurements. That is, only the higher rate of sodium phosphate when used with lime was more efficient than lime alone. The differences produced by applications of rock phosphate were not so obvious as those produced by lime or by sodium phosphate. A statistical analysis was made of the data from the check soil and the six rock phosphate soil treatments. The data in the summary table (16) of this analysis show that no significant mean difference in content of exchangeable hydrogen was effected by application of rock phosphate.

The amounts of exchangeable calcium in the variously treated soils are given in table 17.

Only those treatments which included lime show an increase in the exchangeable calcium content of the soil. Much of this was probably due to soluble calcium dissolved by the ammonium acetate. The data in table 4 where the results by the Schollenberger method are compared with those obtained by the alcoholic potash method indicate that this was the case. Less exchangeable

Table 16

Analysis of Variance of Exchangeable Hydrogen Content  
of Grundy Silt Loam Treated with Different Amounts of Rock  
Phosphate

Source of Variation	D.f.	Total Sum of Squares	Mean Square
Total	41	208.82	
Within	21	3.92	0.187
Between means of dates	2	118.92	59.46 **
Between means of treatment	6	22.45	3.74
Interaction	12	63.53	5.29 **

\*\* Mean square highly significant

Table 17

Exchangeable Calcium Content of Grundy Silt Loam by the  
Ammonium-Acetate Method of Schollenberger

Treatment	M.E. Exch. Ca. per 100 gms. soil			
	D A T E			
	: 7-11-33:	: 11-33-33:	: 8-11-34:	Treatment Means
1. A Check	15.30	16.74	12.92	
B	15.30	16.23	12.09	14.76
2. A 500# rock phos.	17.57	15.09	12.71	
B	15.71	15.51	12.71	14.88
3. A 1000# rock phos.	16.54	15.30	12.82	
B	16.12	15.09	12.82	14.78
4. A 1500# rock phos.	16.95	15.71	14.68	
B	15.71	15.50	14.68	15.54
5. A 2000# rock phos.	16.33	17.36	15.09	
B	15.71	16.74	14.99	16.04
6. A 2500# rock phos.	15.30	16.95	14.78	
B	15.30	15.71	15.09	15.52
7. A 3000# rock phos.	15.30	15.71	14.99	
B	15.71	16.12	13.33	16.03
8. A 1000# rock phos.	23.15	22.12	23.36	
B + 4 T. lime	22.74	21.91	23.36	22.77
9. A 2000# rock phos.	24.39	22.94	23.15	
B + 4 T. lime	23.56	21.70	22.94	23.11
10. A $\text{Na}_3\text{PO}_4$ = 1000#	14.88	15.63	14.68	
B rock phos.	15.09	15.63	14.99	15.15
11. A $\text{Na}_3\text{PO}_4$ = 2000#	14.88	16.74	14.88	
B rock phosphate	15.71	17.16	15.09	15.74
12. A $\text{Na}_3\text{PO}_4$ = 1000#	23.25	25.01	22.84	
B + 4 T. lime	23.77	23.15	24.49	23.77
13. A $\text{Na}_3\text{PO}_4$ = 2000#	23.36	23.36	23.15	
B + 4 T. lime	23.36	23.15	22.94	23.22
14. A 4 T. lime	23.36	23.98	22.84	
B	23.15	23.05	23.46	23.31

calcium was found in the limed soils by the alcoholic-potassium-chloride method than by the ammonium acetate method but still there was a noticeable increase in the content of exchangeable calcium in the limed soils over that in the unlimed soils. Whether this increase represents a higher content of exchange calcium resulting from the lime treatment or was merely due to soluble calcium dissolved from the  $\text{CaCO}_3$  by the reagents used in leaching is not known.

There was no significant difference between the exchangeable calcium in the untreated soil and the soils treated with rock phosphate.

That the variation between treatments was not significant is quite apparent in table 18. Yet it may be noted that in the results for July 11, 1934, samples there was a decided trend toward lower exchangeable hydrogen values with increases in the amounts of rock phosphate used.

d. Growth, Yield and Calcium Content of Sweet Clover and Available Phosphorus and Nitrate-nitrogen Content of the Soil

There was a noticeably higher growth and greener color of sweet clover where rock phosphate was used than on the untreated soils. There was some tendency for the growth to be more vigorous as the rates of application increased. A very poor stand and stunted growth of clover was obtained on soils treated with applications of sodium phosphate alone and the lime alone in contrast to all the other treatments. Sodium phosphate with

Table 18

Analysis of Variance in Exchangeable Calcium Content  
of Grundy Silt Loam  
Treated with Different Amounts of Rock Phosphate

Source of Variation	D.f.	Total Sum of Squares	Mean Square
Total	41	71.91	
Within	21	5.95	0.283
Between means of dates	2	41.77	20.885 **
Between means of treatment	6	8.22	1.37
Interaction	12	15.97	1.33

\*\* Mean square highly significant



lime and rock phosphate with lime produced only a fair growth which was not as good as those of some of the soils receiving higher rates of rock phosphate alone. Later all the soils receiving some form of phosphate supported sweet clover crops of about equal vigor, whereas, the untreated soils and the soils receiving lime only produced about equally poor crops, quite obviously below the average of the phosphate treated soils. However, differences in color were quite noticeable. The sweet clover in one of the untreated soils was light green but the clover in the other one was normal. Clover in all the soils receiving different amounts of rock phosphate either alone or in combination with lime showed no chlorosis. The clover in the other treated soils including those receiving different amounts of sodium phosphate either alone or with lime and the soils receiving lime alone all showed distinct chlorosis. A few weeks later practically all the chlorosis had disappeared.

The first cutting of hay was made on June 11 and the second on August 5. The average dry weights of these cuttings are given in table 19. The data for the first seven treatments were analyzed statistically. The data obtained are presented in table 20 A.

The mean square between treatments is shown to be significant but not highly significant, indicating that the average yields for these treatments may be expected to vary significantly.

In order to test the significance of the variability between individual treatments, the least mean difference which could be considered highly significant was found to be 0.99 gm. Likewise,

Table 19

The Growth and Yield of Sweet Clover and the Calcium Content of Sweet Clover on Grundy Silt Loam

Treatment	:Mar. 7:	:March 22	:Yield in :% Ca in	:9 gms. :Sw.Cl.	:Ave. of :Ave. of	:1st & 2nd:1st & 2nd
	:Height:	:Height	:Color	:cuttings	:Cuttings	
1 A. Check	++	++++	Lk. green	18.55	2.212	
B.	++	+++	Lt. "			
2 A. 500# rock phos.	++	+++++	Lt. "	22.47**	2.096	
B.	++++	+++++	Dk. "			
3 A. 1000# rock phos.	+++	+++++	Dk. "	19.17	2.180	
B.	++++	+++++	Dk. "			
4 A. 1500# rock phos.	++++	+++++	Dk. "	20.47**	2.170	
B.	++++	+++++	Dk. "			
5 A. 2000# rock phos.	+++++	+++++	Dk. "	22.93**	2.088	
B.	++++	+++++	Dk. "			
6 A. 2500# rock phos.	+++++	+++++	Dk. "	24.97**	2.291	
B.	+++++	+++++	Dk. "			
7 A. 3000# rock phos.	++++	+++++	Dk. "	24.95**	2.026	
B.	++++	+++++	Dk. "			
8 A. 1000# rock phos. + 4 T. lime	+	+++++	Pale gr. to yel.	25.72*	2.392	
B.	+	+++++	Pale gr. to yel.			
9 A. 2000# rock phos. + 4 T. lime	+	+++++	Pale gr. to yel.	26.68*	2.362	
B.	++	+++++	Pale gr. to yel.			
10 A. Na <sub>3</sub> PO <sub>4</sub> = 1000#	++++	+++++	Dk. green	26.51	1.998	
B. rock phos.	++++	+++++	Dk. "			
11 A. Na <sub>3</sub> PO <sub>4</sub> = 2000#	+++	++++	Dk. "	26.81	2.014	
B. rock phos.	++++	+++++	Dk. "			
12 A. Na <sub>3</sub> PO <sub>4</sub> = 1000# rock phosphate	+++	+++++	Med. "	28.53**	2.282	
B. + 4 T. lime	++++	+++++	" "			
13 A. Na <sub>3</sub> PO <sub>4</sub> = 2000# rock phosphate	++++	+++++	" "	31.79**	2.328	
B. + 4 T. lime	++	+++++	Dk. green			
14 A. 4 T. lime	+	+++	Lt. "	28.87	2.438	
B.	+	++++	Lt. "			

\* Significantly greater than the yield of any treatment above it in column.

\*\* Highly significantly greater than the yield of any treatment above it.

Table 20

Analysis of Variance of Sweet Clover Yields on Grundy  
Silt Loam

Source of variation	Degrees of freedom	Sum of squares	Mean Square
A.			
Untreated Soil and Soils Treated with Rock Phosphate Only			
Total	13	424.92	
Within--treatment groups	7	99.26	14.18
Between means of treatments	6	325.65	54.88*
B.			
Entire 14 treatments of Experiment II			
Total	27	1813.0	
Within--treatment groups	14	298.8	21.34
Between means of treatments	13	1514.9	116.48**

\* Significant  
\*\* Highly significant

the least mean significant difference was 0.64 gm. The analysis of the data for the entire experiment (table 20 B) showed that the mean square between treatments was highly significant. The least highly significant mean difference was 3.83 gm. and the least significant mean difference was 2.53 gm.

The rock phosphate treated soils, except the 1500 pound per acre treatment, produced highly significant increases in yield. Although some variability occurred in the results from the 500, 1000, 1500 and 2000 pound rates, rates of 2500 and 3000 pounds per produced mean yields greater than any of the other treatments by highly significant amounts. Likewise, the 2000 pound rate caused a significant increase in mean yield above all the lesser rates except the 1000 pounds per acre. All the treated soils yielded more sweet clover than the untreated soil. Hence, it may be said that application of rock phosphate increased the yield of sweet clover in most cases to a highly significant extent and that there was a tendency for this increase to be proportional to the amount of rock phosphate added. The soils receiving lime or sodium phosphate produced mean yields of sweet clover significantly greater than that on the untreated soils. Rock phosphate with lime increased the yield over that from equivalent amounts of rock phosphate alone by significant amounts. However, 1000 or 2000 pounds of rock phosphate per acre with 4 tons of lime per acre caused an increase in yield significantly higher than that with the 2500 and 3000 pound per acre rates of rock phosphate alone. One thousand and 2000 pounds of rock phosphate per acre

with 4 tons of lime and the 1278 and 2557 pound applications of sodium phosphate did not differ from each other significantly in respect to the mean yields of sweet clover.

The highest mean yield of sweet clover was produced by 2557 pounds of sodium phosphate in combination with lime. This yield was greater than that of either the lime alone or the lime plus 1278 pounds of sodium phosphate pots by significant values and greater than the yields of any of the other treatments by highly significant amounts.

All three of the last named treatments produced yields significantly greater than those resulting from any other treatment.

It is interesting to note that the treatment producing the highest yield, 2557 pounds of sodium phosphate, with 4 tons of lime, also produced the highest pH and the lowest lime requirement.

No consistent difference in the average per cent of calcium was found in the sweet clover hay of these two cuttings.

Since the nitrate nitrogen content of the soil has been known to vary with reaction as shown by Peterson (56), nitrate nitrogen determinations were made on April 4, after the soil had been kept at uniform moisture content for 16 months. For the treatments of rock phosphate alone there was considerable variability in results with no definite trends that could be connected with treatment except that the soil having the highest application of phosphate, 3000 pounds per acre, also had the

highest content of nitrate nitrogen. The nitrate content of this soil was 161.9 p.p.m. as compared with 153.8 p.p.m. in the untreated soil. The results of this test are given in table 21.

3. The Effect of Rock Phosphate, Superphosphate, Ammo Phos "A", Ammoniated Phosphate and Treble Superphosphate on the Reaction of Three Acid Iowa Soils

In this study Tama silt loam from Marshall County, Iowa, Carrington silt loam from Grundy County, Iowa, and Grundy silt loam from Harrison County, Missouri, were used. The Tama silt loam had a lime requirement of three tons of limestone per acre by the potassium-thiocyanate method. A typical Carrington silt loam which had a lime requirement of three tons per acre was obtained from the Iowan Drift soil area. The Grundy silt loam had a lime requirement of three tons per acre. It was taken about fifty miles south of the sample of Grundy silt loam used in Experiment 2. It differed from the Grundy silt loam used in Experiment 2 in that it occurred on the top of a long narrow ridge which broke off sharply into slopes of Lindley as is typical of that part of northern Missouri, whereas, the sample of Grundy silt loam used in Experiment 2 was found on a very broad flat ridge and had a much deeper A horizon.

Samples of these three soils were taken in September, 1934, sieved and placed in gallon pots in the greenhouse at the rate of 6000 gms. per pot. Pots of each soil were treated in triplicate with rock phosphate, superphosphate, Ammo Phos "A", ammoniated phosphate, and treble superphosphate in equivalent

Table 21

The Available Phosphorus and Nitrate Nitrogen  
Content of Grundy Silt Loam

Treatment	: Available *: Phosphorus : : p.p.m. :	Nitrate **: Nitrogen p.p.m.
1. Check	32.20	153.8
2. 500# rock phosphate	55.92	167.7
3. 1000# rock phosphate	82.50	168.0
4. 1500# rock phosphate	115.34	150.6
5. 2000# rock phosphate	142.36	156.3
6. 2500# rock phosphate	168.67	155.3
7. 3000# rock phosphate	194.03	161.9
8. 1000# rock phosphate + 4 T. lime	96.10	288.3
9. 2000# rock phosphate + 4 T. lime	147.16	277.3
10. $\text{Na}_3\text{PO}_4$ = 1000# rock phos.	69.58	154.0
11. $\text{Na}_3\text{PO}_4$ = 2000# rock phos.	102.37	181.8
12. $\text{Na}_3\text{PO}_4$ = 1000# rock phos. + 4 T. lime	89.20	299.6
13. $\text{Na}_3\text{PO}_4$ = 2000# rock phos. + 4 T. lime	132.37	310.8
14. 4 T. lime	41.83	314.0

\* Treatment means of measurements made 1-11-33, 7-11-33 and 11-23-33.

\*\* Treatment means of measurements made on 4-11-34.

amounts of  $P_2O_5$  on the basis of 300 pounds of 20 per cent superphosphate per acre, except for the rock phosphate which was added at the rate of 1000 pounds per acre. A similar series was also set up wherein the amounts of phosphate added were increased by five times in every case. The soils were first watered on October 7, 1935, and although care was taken to prevent puddling and to keep the moisture content uniform the soil moisture was allowed to fluctuate in an attempt to simulate field conditions.

The rock phosphate used was the same as that used in Experiment 2. The superphosphate used was the same as that used in Experiment 1. The Ammo Phos"A" had a guaranteed analysis of 11 per cent N and 47 per cent  $P_2O_5$  and was furnished by the American Cyanamid Company. Anaconda ammoniated phosphate containing 52.3 per cent total  $P_2O_5$  and 13.2 per cent ammonia was used. The treble superphosphate contained 48 per cent total  $P_2O_5$  and was also furnished by the Anaconda Company.

Samples from each pot were taken on April 25, 1936, almost seven months after treatment, dried, and analyzed for pH by the quinhydrone electrode method. The results obtained are presented in table 22. An analysis of variance of the data was made and the results obtained are given in tables 23 and 24.

The data in the tables show that there was considerable variation in pH of the soils treated with the different fertilizers. There was a highly significant difference in the pH of the soils treated with the different fertilizers and the interactions between treatment and soil type, treatment and rate of application, and rate of application and soil type were also highly significant.



Table 22

The pH of Grundy Silt Loam, Carrington Silt Loam and Tama  
Silt Loam Treated with Different Phosphate Fertilizers at  
Two Rates of Application

Treatment	* Normal Rate			5 Times Normal Rate			Treat- ment Means
	Carrington:	Grundy :	Tama	Carrington:	Grundy :	Tama	
	Silt Loam	Silt Loam	Silt Loam	Silt Loam	Silt Loam	Silt Loam	
Check	4.67	5.36	4.76	4.75	5.28	4.80	4.94
	4.74	5.36	4.78	4.72	5.30	4.74	
	4.73	5.39	4.79	4.74	5.35	4.73	
Rock Phosphate	4.80	5.33	5.10	4.93	5.68	4.89	5.12
	4.78	5.40	4.96	4.93	5.63	4.89	
	4.80	5.46	4.96	4.98	5.68	4.89	
Superphosphate	4.79	5.30	4.70	4.63	5.16	4.74	4.90
	4.79	5.30	4.80	4.66	5.22	4.73	
	4.79	5.30	4.76	4.68	5.17	4.71	
Ammono Phos "A"	4.70	5.26	4.81	4.59	5.44	4.67	4.92
	4.70	5.27	4.76	4.63	5.44	4.80	
	4.72	5.30	4.78	4.61	5.39	4.76	
Ammoniated Phosphate	4.63	5.22	4.81	4.58	5.31	4.67	4.89
	4.69	5.24	4.82	4.64	5.32	4.71	
	4.70	5.21	4.82	4.61	5.34	4.70	
Treble Superphosphate	4.78	5.31	4.80	4.67	5.51	4.82	5.01
	4.85	5.31	4.86	4.79	5.54	4.82	
	4.84	5.29	4.90	4.77	5.56	4.82	

\*Fertilizer applied in amounts equivalent to 300# superphosphate per acre  
except for flat application of 500# rock phosphate per acre.

Note: Least highly significant mean difference is 0.029 pH.

Least significant mean difference is 0.022 pH.

Table 23

Analysis of Variance in pH of Grundy Silt Loam, Tama Silt Loam and Carrington Silt Loam Treated with Different Phosphate Fertilizers

Source of Variation	: :D.f.: :	: Total Sum : of Squares :	: Mean : Square :
Total	107	9.6821	
Within	72	.0792	.0011
Between means of treatments	5	.6633	.1327 **
Between means of types of soil	2	8.4745	4.2372 **
Between means of rules of application	1	0	0
Treatment and soil type	10	.0630	.0063 **
Treatment and rate	5	.0970	.0194 **
Rate and soil type	2	.1221	.0610 **

$$s_{md} = \sqrt{2 \left( \frac{.0011}{18} \right)} = .01106$$

$$M_D = s_{md} \times 1.994 = .02205 \text{ least significant mean difference}$$

$$M_D = s_{md} \times 2.648 = .02929 \text{ least highly significant mean difference}$$

\*\* Mean square highly significant

Table 24

Analysis of Variance in pH on Three Iowa Soils Treated with Phosphate Fertilizers at Normal Rates of Application

Source of Variation	D.f.	Total Sum of Squares	Mean Square
(A)			
Total	53	3.6020	
Within	36	.0448	.0012
Between means of treatments	5	.1516	.0303 **
Between means of soil types	2	3.3153	1.6577 **

(B)

Analysis of Variance in pH on Three Iowa Soils Treated with Phosphate Fertilizers at 5 Times Normal Rate of Application

Total	53	6.0802	
Within	36	.0344	.0010
Between means of treatments	5	.6088	.1218 **
Between means of soil types	2	5.2814	2.6407 **

\*\* Mean square highly significant

Testing mean square of between means of treatments of normal rate against 5 times normal rate the F value for .1218 is not significant  
.0303

## DISCUSSION

In Experiment I it was shown definitely by measurements of pH and base exchange properties that rock phosphate decreased the acidity of the soil and that superphosphate in ordinary rates of application increased the acidity of the soil. Whether these changes are large enough to be important in crop growth depends largely on the crop and the properties of the soil on which it is grown. In this respect it is interesting to note that although the increase in mean pH from 5.79 to 5.85 due to 2000 pounds of rock phosphate was highly significant statistically, it was still very much below the pH value of 7.002 produced by 4000 pounds of limestone, the amount needed to neutralize this particular soil according to the Truog test.

With Grundy silt loam as with Carrington loam, rock phosphate was found to decrease the acidity by a highly significant amount when measured by pH and the Hardy-Lewis lime requirement methods. Although each 400 pound increase in rate per acre did not always result in a highly significant decrease in acidity, there was a trend for the higher amounts to be more effective in neutralizing the acidity of the soil. However, rock phosphate did not produce a significant difference in reaction of Grundy silt loam as measured by base exchange capacity, exchangeable hydrogen, or degree of saturation. Therefore, it would appear that the determination of replaceable hydrogen is not as accurate an index of soil acidity as is the Hardy-Lewis test

for lime requirement or the quinhydrone electrode method of determining pH. Although rock phosphate decreased the acidity of Grundy silt loam by highly significant amounts during the 20-month period, this does not show the exact importance of these differences agriculturally.

The cropped series of soils was set up in order to get some sort of a check on the agricultural importance of the variations in reaction caused by different amounts of rock phosphate. Sweet clover was used because of its high sensitivity to acidity.

Observations on growth of the clover revealed an early stimulating effect from all rates of application of rock phosphate although there was not a great difference between treatments.

An increase in yield was obtained wherever rock phosphate was used, the two highest rates of application being associated with the highest yields.

An analysis of variance of the yields for the check soils and the soils receiving only rock phosphate gave a least highly significant mean difference of 0.99 gms. and a least significant mean difference of 0.64 gms. Testing with these values highly significant differences were found between the means of the untreated soil and all those treated with rock phosphate, except that of the 1500 pound application. The mean yields of the 2500 and 3000 pound applications were the largest, the increase in yield from these two treatments over those of all other rock phosphate treatments being highly significant in every case.

In the nitrate-nitrogen curve of figure 1 no constant relationship was found between the amount of rock phosphate applied and the amount of nitrate-nitrogen in the soil. This shows that increased nitrate-nitrogen content as the result of additions of rock phosphate was not an important factor in the response of sweet clover.

Any response from rock phosphate may be due to several things but probably chiefly to the phosphate and calcium furnished as plant nutrients and to the acid neutralizing power of the phosphate fertilizer.

A measure of the available phosphorus in the soil following different applications of phosphate can be expected to furnish an indication of the extent to which any response to the treatments in question may be due to the actual phosphorus supplied.

The amount of available phosphorus in the various soils at one month, six months and eleven months after the experiment was started are plotted against the different treatments, figure 1.

The data show that the available phosphorus content of the soil was almost a direct function of the amount of rock phosphate added. Because of this it is difficult to determine the effect on plant growth of other elements supplied to the soil by the phosphate. The possible effect of the calcium ion itself as emphasized by Albrecht (2) further complicates the interpreta-

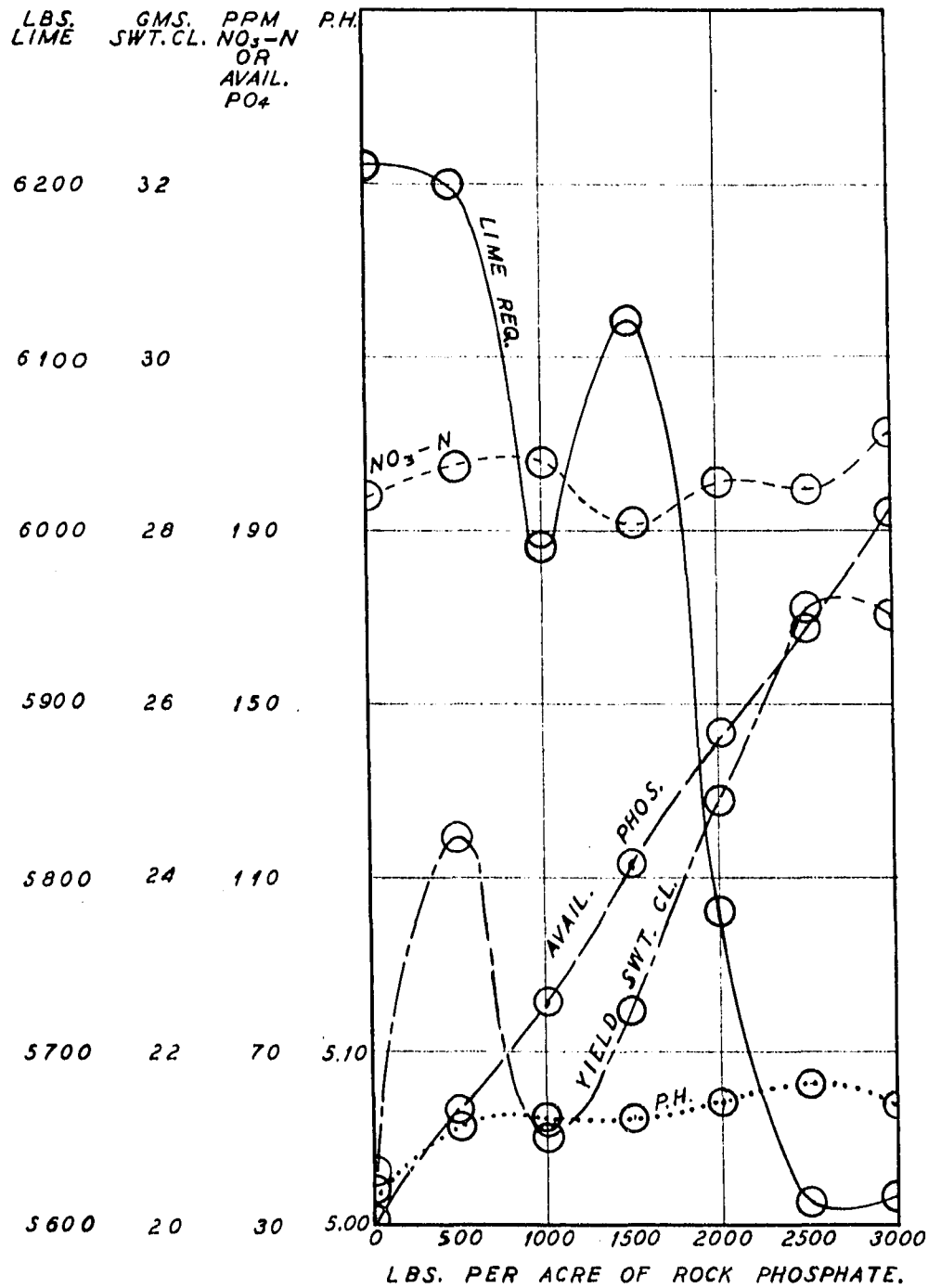


Fig. 1. Effect of Rock Phosphate on Grundy Silt Loam.

tion of crop response.

The relationships between reaction, nitrate-nitrogen content, available phosphate content and yield of sweet clover are shown in figure 1.

As pointed out previously there was a highly significant increase in basicity following any applications of rock phosphate of 500 pounds or more per acre with a decided trend upward with increased rates of application. Likewise, the lime requirement in general decreased with increased size of applications of rock phosphate, especially with increments of 500 pounds beyond the 1500 pound rate. Also the yield of sweet clover for the 500 and the 1000 pound rates of phosphate increased with increased amounts of rock phosphate added.

How much of the increased yield was due to the soluble phosphate added and how much to the correction of the acidity was not determined. That the soluble calcium may not be a great factor is indicated by the fact that no significant difference in the content of exchangeable calcium was found in any of the soils treated with the different amounts of rock phosphate or between the untreated soil and any of the phosphated soils. Exchangeable calcium is not synonymous with available calcium and there may be differences in exchangeable calcium content of the soils significant to sweet clover culture not determined by the methods used.

That soluble calcium was not supplied by rock phosphate in amounts sufficient to affect the growth of sweet clover was in-



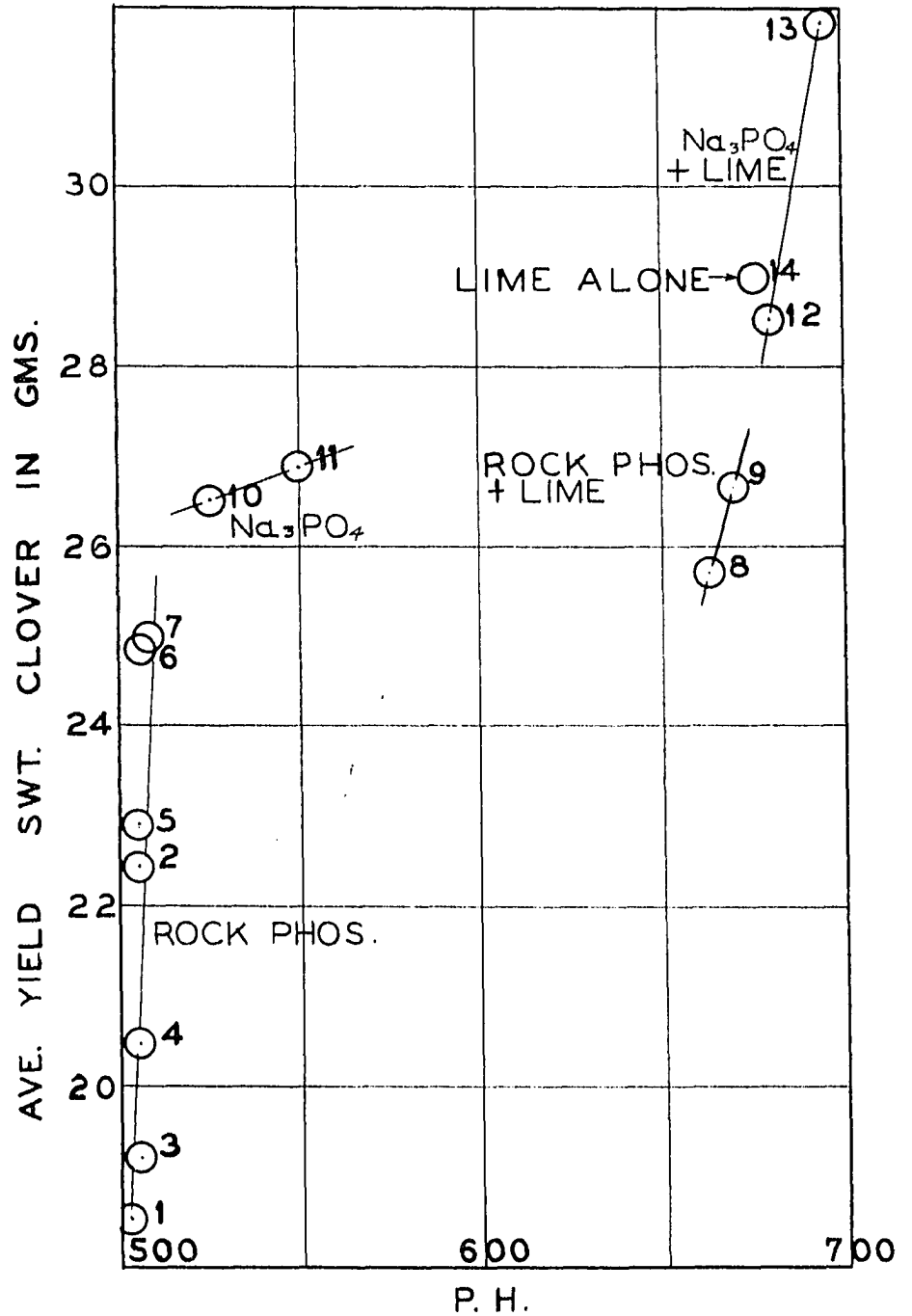


Fig. 2. The Relation of pH to Yield of Sweet Clover.

indicated by the fact that no difference was found in the calcium content of the sweet clover which could be shown to relate in any way to the amount of rock phosphate added. However, the untreated Grundy silt loam contained a fairly high amount of exchangeable calcium, possibly enough to satisfy the nutritional needs of the sweet clover.

In order to compare the relative value of these different variables in regard to their effect on sweet clover, figures 2, 3 and 4 were drawn with yield plotted against pH, exchangeable calcium, and available phosphorus, respectively.

It is apparent that an increase in available phosphorus in the soil and an increase in the crop yield accompanied increases in the amount of phosphate applied, figure 4. Except for 4 tons of  $\text{CaCO}_3$  alone, the nutritional value of the phosphate added seemed to be an important variable with soils of similar pH and exchangeable calcium content. However, the kind of phosphate and the addition of lime with the phosphate affect the yield noticeably.

Treatments number 12, 10, 8 and 3, all receiving amounts of phosphate equivalent to that of 1000 pounds of rock phosphate did not show much variation in the amount of available phosphate in the soil following treatment but showed large differences in yield of sweet clover. This variability is greatly affected by the type of treatment, that is, sodium phosphate with lime and lime alone produced the highest yields, sodium phosphate the next highest, rock phosphate with lime the next and rock phosphate alone the least of the treated soils.

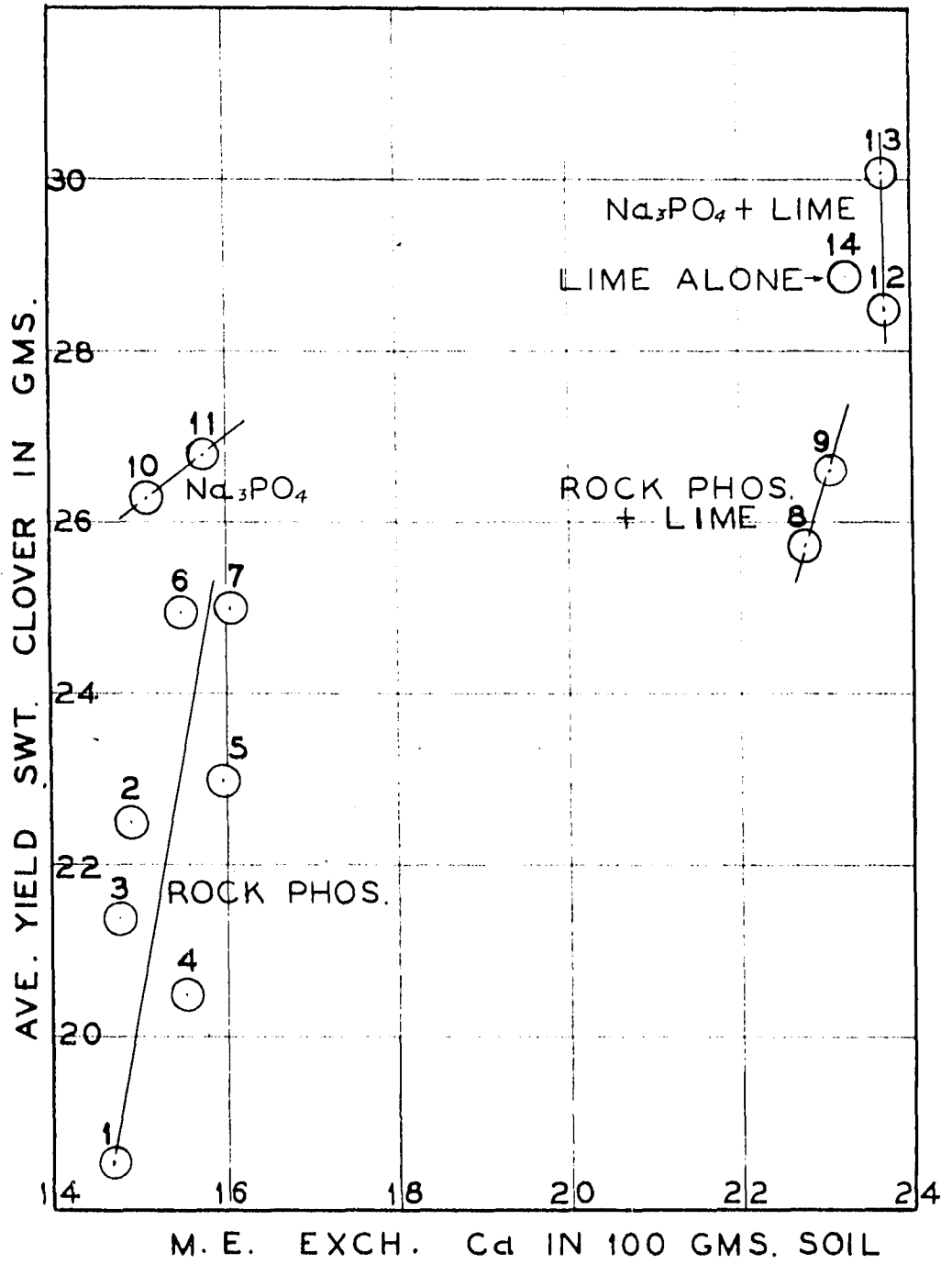


Fig. 3. The Relation of Exchangeable Calcium to Yield of Sweet Clover.

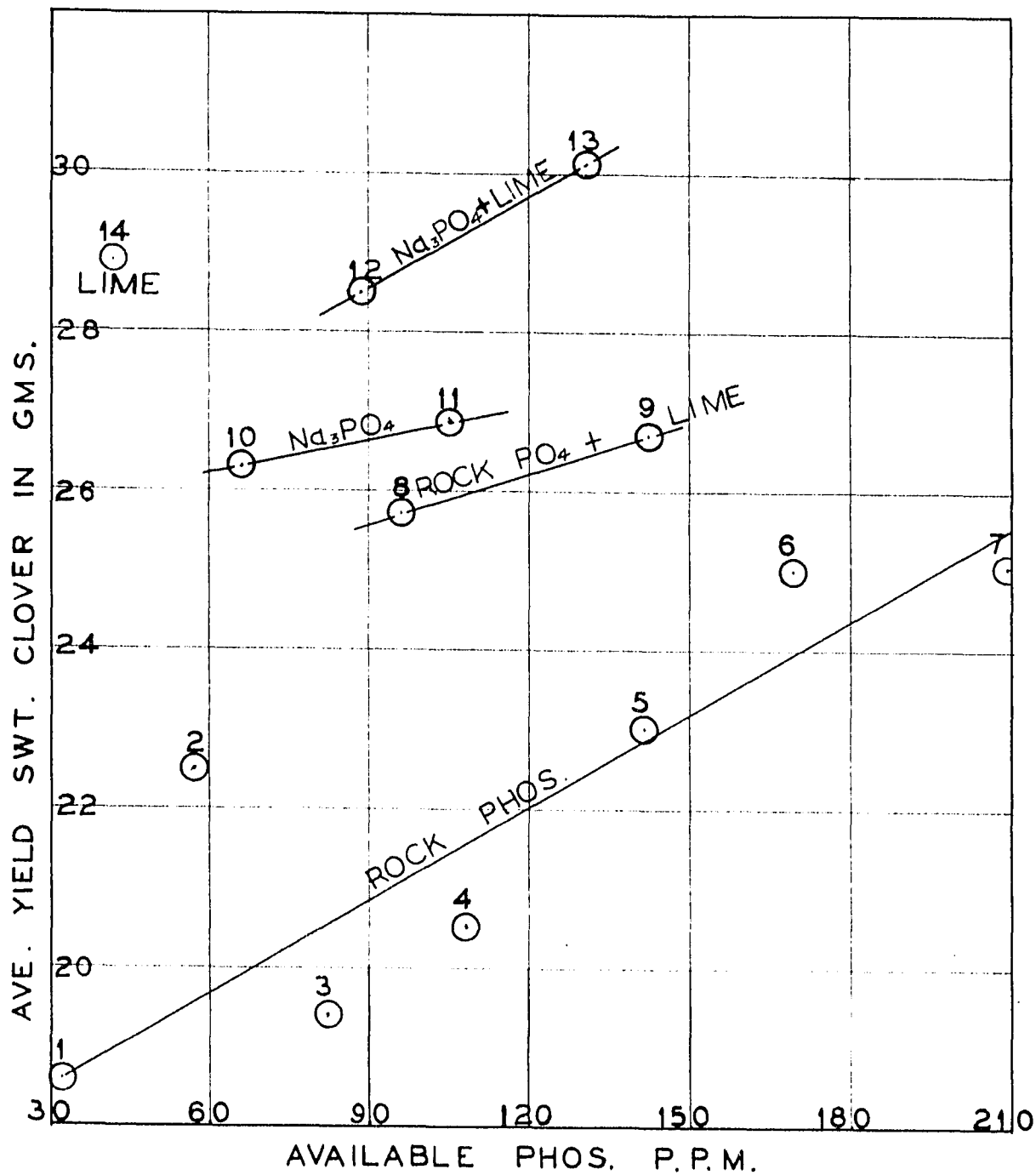


Fig. 4. The Relation of Available Phosphorus to Yield of Sweet Clover.

When phosphate was added in amounts equivalent to 2000 pounds of rock phosphate per acre on the bases of  $P_2O_5$  content, the amount of available phosphorus in the soil and the yield increased over that of the 1000 pound rate in every case. However, figure 4 shows that all soils contained about the same amount of available phosphorus as that treated with the 2000 pounds per acre application of rock phosphate. This shows that the applications of  $CaCO_3$  with the phosphates did not depress the availability of the phosphorus. In figure 4 it is also apparent that yield was affected differently by sodium phosphate than by rock phosphate and that lime had an influence on yield. Since the different combinations of fertilizers do not produce the same yields even when the amounts of available phosphate resulting from the treatments are approximately the same, it is apparent that other factors than the available phosphate supplied are affecting the yield of the sweet clover.

The four soils containing the largest amount of available phosphorus produced only medium yields of sweet clover indicating further that the nutritional effect of the phosphorus accounts for only part of the response of sweet clover to the different treatments.

The relation between pH and yield of sweet clover is shown in figure 2. The data in the graph show that increases in amounts of phosphate were generally accompanied by increases in pH and in yields of sweet clover. Since increased available phosphorus content of soil also accompanied larger applications of phosphate, the difficulty of determining just how much the

yield of sweet clover depends on the nutritional effect of the phosphate and how much on the neutralizing power of the fertilizer is apparent. Nevertheless, there is very good evidence that reaction is the more important variable. The data in figure 2 show that pH was a very important influence in determining crop response. The treatment that produced the highest pH of the soil also produced the largest yield of sweet clover. Likewise, all of the soils having a high pH produced high yields of sweet clover. The soil receiving four tons per acre of lime alone had the third highest pH value and the second highest yield, although it was next to the lowest in available phosphorus.

The soils that received rock phosphate and 4 tons of  $\text{CaCO}_3$  per acre did not yield as well as the soil that received only 4 tons of  $\text{CaCO}_3$ . The lower yielding soils had significantly lower pH values.

The sodium phosphate treated soils outyielded the rock phosphate treated soils when the phosphate was applied alone or with lime and in almost every case the reaction of the soils receiving the sodium phosphate was less acid than that of the rock phosphate soils by a highly significant amount measured by pH or by lime requirement.

An outstanding feature of figure 2 is the marked beneficial effect of sodium phosphate on the yield of sweet clover. The highest yield was obtained with 2557 pounds of sodium phosphate and lime. The application of 1457 pounds of sodium phosphate

and lime produced the third highest yield. The two applications of sodium phosphate alone, numbers 10 and 11 of figure 2, produced yields corresponding to rock phosphate with lime and higher yields than those of any of the rock phosphate treatments.

The marked effect of sodium phosphate on the pH of the soil indicates the value of pH as a factor in the yield of sweet clover. However, it does not fully account for the value of sodium phosphate as a sweet clover fertilizer. The soils receiving lime and rock phosphate had much higher pH values than did the soils receiving only sodium phosphate but the yields did not differ noticeably.

Yields of sweet clover plotted against millequivalents of exchangeable calcium per 100 gms. of soil, figure 3, shows the high correlation between the exchangeable calcium content of the soil and the pH of the soil. The soils having a very high pH also contained high amounts of exchangeable calcium.

Why the very large increases in pH and content of exchangeable calcium associated with the limed soils did not cause greater increases in yield than they did is not known. The high figures for exchangeable calcium may be due to calcium dissolved from calcium carbonate by the ammonium acetate. The rather small increases in yield with large increases in pH following liming may be due to the interaction between pH and other variables affecting yield. Large amounts of soluble phosphorus or calcium in the soil may augment the effect of pH on yield. In the case of the sodium phosphate treated soils the sodium may cause the increased yield of sweet clover previously pointed out.

The sodium phosphate treated soils produced higher yields of sweet clover than the corresponding rock phosphate treated soils. The pH of the sodium phosphate treated soils was significantly higher than that of the rock phosphate treatments but the differences in the content of exchangeable calcium were small and not significant. This relationship was also apparent where lime was added with the different phosphates. These results indicate that exchangeable calcium was not an important factor in the yield of sweet clover unless the amount of exchangeable bases was associated with pH of the soil.

A multiple correlation was made of the pH, the p.p.m. nitrate-nitrogen, the M.E. of exchangeable calcium, the p.p.m. of available phosphorus, the per cent calcium in the crop and the yield of sweet clover in grams. The results are given in table 25.

The data show that the amount of available phosphorus in the soil was not significantly correlated with yields of sweet clover. This does not prove, however, that the beneficial effect of rock phosphate on sweet clover was due to the lime supplied by the rock phosphate.

The data in the graph show that although the correlation was low, increased available phosphorus followed an increase in yield. Available phosphorus had some effect, but apparently the effect of the phosphorus was overshadowed by differences due to reaction.

The correlation between yield and pH, nitrate-nitrogen content and exchangeable calcium content was highly significant.



Table 25

The Correlation of pH, Exchangeable Hydrogen, Exchangeable Calcium, Nitrate Nitrogen and Available Phosphorus Content of Grundy Silt Loam and of the Yield and Calcium Content of Sweet Clover

	: :Nitrate-: :Nitrogen:	: : Exch. : : H :	: : Exch. : : Ca. :	: : Avail. : : P. :	: : Yield : : Sw. Cl. :	: : % Ca. in : : Sw. Cl. :
	**	**	**		**	**
pH	.9880	-.9610	.9852	-.0566	.8632	.7454
Nitrate N.		**	**		**	**
		-.9654	.9824	-.1000	.8006	.7816
Exch. H.			**		**	**
			-.9410	.1674	-.8149	-.7603
Exch. Ca.				**	**	**
				.0107	.7736	.7839
Avail. P.					-.0774	-.1045
Yield Sw. Cl.						.3173

\*\* Highly significant correlation

.53 least significant correlation factor.

.66 Least highly significant correlation factor.

#### Beta Values

	Beta	r
Beta yield x Avail. P.	= +.0303	-.0774
" " x % Ca. in Sw. Cl.	= -.6892	+.3173
" " x Exch. H.	= +.5136	-.8149
" " x Nitrate N.	= +.1684	+.8006
" " x Exch. Ca.	= -.5667	+.7736
" " x pH	= 1.2500	+.8362

The correlation between yield and exchangeable hydrogen was negative and highly significant.

The pH was correlated to a highly significant extent with nitrate-nitrogen, exchangeable hydrogen and exchangeable calcium content of the soil and with per cent of calcium in the plant. The correlation between the nitrate-nitrogen content of the soil, pH, exchangeable hydrogen, exchangeable calcium of the soil and per cent calcium in the plant was highly significant in every case. Likewise, exchangeable hydrogen shows highly significant correlation values when compared with pH, nitrate-nitrogen, and exchangeable calcium of the soil and with per cent calcium in the plant, the correlation in every case being negative since an increase in exchangeable hydrogen represents a decrease in pH.

The amount of exchangeable calcium was also correlated significantly with the per cent of calcium in the plant. On the other hand, available phosphate did not show a significant correlation with any of the variables studied.

The yield of clover was correlated to a highly significant extent with every variable measured, except the per cent of calcium in the plant and the amount of available phosphorus in the soil. All the variables affecting yield to a highly significant extent also showed a highly significant correlation with each other, namely, pH, nitrate-nitrogen content, content of exchangeable hydrogen and content of exchangeable calcium in the soil. This shows the higher interrelation of these factors

to each other and emphasizes the difficulty of determining which of these factors was responsible for the way in which phosphates may substitute for lime.

The very marked increase in both exchangeable calcium and pH and equally marked decrease in exchangeable hydrogen following applications of lime probably accounts for a large degree of the correlation between these variables. Hence, it may not be fully justifiable to say that increased yield with increased rates of rock phosphate were due to increases in either pH or exchangeable calcium. Nevertheless, any treatment which supplied exchangeable calcium to the soil or decreased acidity must have had some effect on yield. Likewise, it is highly probable that the measurable decrease in acidity following the use of rock phosphate indicates that rock phosphate may substitute in some measure for lime in supplying calcium for the growth of sweet clover.

In a simple correlation the nitrate-nitrogen content of the soil was significantly correlated with the yield of sweet clover. However, in the multiple correlation there was no significant correlation, that is, when the other factors affecting the yield of sweet clover were considered it was found that the nitrate-nitrogen content did not affect the yield of sweet clover significantly.

From the other Beta values in the multiple correlation, table 25, it is evident that pH had the largest effect on yield of sweet clover. This was the only single variable measured which was significantly correlated with yield. The exchangeable calcium

had the next most important effect on yield although not significant. Exchangeable hydrogen was next in its correlation with yield of sweet clover. The effect of the other variables on yield when considered independently had less significance.

Rock phosphate, sodium phosphate, lime, rock phosphate with lime and sodium phosphate with lime increased the yield of sweet clover significantly in most cases and in some cases to a highly significant extent. The fact that the yields of sweet clover from the soils treated with 2500 and 3000 pound per acre of rock phosphate closely approximated those of rock phosphate with lime indicates the value of rock phosphate in acid soils.

Sodium phosphate with lime and lime alone produced the highest yields and gave the highest pH values. Sodium phosphate alone was more effective than rock phosphate in increasing the pH of the soil. This indicates the importance of pH upon the yield of sweet clover and this importance is further emphasized by the highly significant Beta value representing the correlation between pH and the yield of sweet clover. That pH was the only variable studied which showed such a high correlation indicates that changes in pH caused by the different treatments may be partly if not largely responsible for the increase in yield of sweet clover following application of rock phosphate on acid Grundy silt loam.

High exchangeable calcium was associated with the high lime series but not much variability in exchangeable calcium within the lime series or within the unlimed series can be associated

with differences in amounts of phosphate used. This fact, together, with the high response to sodium phosphate, which adds no calcium to the soil, and the lack of significant differences in the mean calcium content of sweet clover grown on the different rock phosphate treated soils show that not enough calcium was added by rock phosphate to be a factor in yield. The fact that the method for determining exchangeable calcium was not entirely satisfactory where high lime soils were concerned and that exchangeable calcium and available calcium may not be the same must be considered.

That available phosphorus was a very important factor in yield of sweet clover especially with the same kind of phosphate where the pH values were of the same order is apparent from figure 4. This may explain much of the variability in mean yield of sweet clover between increments of phosphate of the same kind and with the same amount of lime applied.

That phosphorus alone was not the most important factor is shown by the high yields obtained on soils of high pH values but with low available phosphorus content, by the low yields of some soils with high phosphorus content, and by the general lack of correlation between available phosphorus and yield.

It appears, then, that pH was the most important factor in determining sweet clover growth.

Apparently the total effect of all these factors depends on the interaction between all the different factors as well as on the effect of any one of them individually. The data and the design of the experiment were not adequate to permit of definite

conclusions. Nevertheless, the different variables plotted against yield of sweet clover, the results of the statistical analysis of the data and the correlations found between the different variables showed certain apparent relationships.

There was a consistent significant response of sweet clover to small but significant changes in pH. When pH was isolated from the other variables it still had a correlation to yield that was highly significant. This was not true of the other factors studied. Likewise, increases in pH were found significantly associated with increases in the amounts of phosphate added.

This seems to show that rock phosphate increases the yield of sweet clover by neutralizing some of the soil acidity.

It is apparent that increases in yield of sweet clover were associated with increases in the amounts of available phosphorus in the soil for soils having the same range of pH and the same kind of phosphate added. However, it must be pointed out that there was no clover and available phosphorus in the soil and that available phosphorus was not the most important factor in determining sweet clover growth.

The total variation in pH between the two rates of application in Experiment 3 was 0. (Table 23). At first glance this would seem to indicate that there was no difference in effect on pH between the normal rate of application of the fertilizers and five times the normal rate. That this is not the case is indicated by the highly significant variability in the interaction of treatment on rate and by the much greater range in the pH of

the different treatments at the five times normal rate as compared with the range in pH between treatments at the normal rate. In order to test this more thoroughly a separate analysis of variance of the pH data at the normal rate and at the five times the normal rate of application was made and is shown in table 24.

Testing the variance between treatments at the normal rate and at five times normal rate (table 24), the variance of the larger rate is found to be about four times greater but this is not a significant amount. In other words the increase in variation of pH between treatments with increased rate of application may be due to chance. This does not justify testing the significance of the treatment means of each rate separately. Because of this the pH readings of all the samples at both rates were averaged for each treatment to get the treatment means.

The least mean difference between the means for each treatment which can be considered highly significant was 0.029 pH. The treatment means given in table 22 show that the rock phosphate increased the pH by a highly significant amount. Superphosphate decreased the pH to a highly significant extent. The mean pH of the soils receiving Ammo Phos "A" did not differ significantly from that of the check soil. The pH of the soil treated with ammoniated phosphate was significantly lower than that treated with the Ammo Phos "A" as well as that of the untreated soil. The treble superphosphate increased the pH of the soil a highly significant amount but did not increase it to nearly

as high pH as did the rock phosphate.

From these results the high neutralizing value of rock phosphate is apparent. It was also shown that treble superphosphate neutralized soil acidity to a measurable extent. The acidic effects of superphosphate, Ammo Phos "A" and ammoniated phosphate are apparent. The highly significant variability in pH due to the effect of soil type on treatment shows that the neutralizing effect of the different fertilizers depended to some extent upon the properties of the different soils. Likewise, the large variance of the interaction between treatment and rate of application showed that the different treatments did not produce the same effect on pH at the two different rates of application. In other words, increasing the rate of application did not result in increases or decreases in pH in exactly the same way at the higher rates of application as at the lower rates of application.

The experimental error in measuring pH was very small. This small variation in pH caused by error made possible the measurement of relatively small differences in pH resulting from treatment or other causes. In the Carrington loam studies of Experiment 1 duplicate samples were taken from each of the duplicate pots for each of five differently treated soils at ten different dates. A total of 200 pH determinations were made. The experimental error or the variance between means of samples of the same treatment at the same date was only .004 pH (table 3) and the least mean difference which was highly significant was 0.053 pH.



In the Grundy silt loam studies of Experiment 2 for 13 dates and 14 treatments in duplicate, a total of 364 determinations were made and the experimental error was only 0.001 pH (table 9). The least mean difference which could be considered highly significant was 0.023 pH. In Experiment 3 with six treatments in triplicate at two different rates and for three different soils, or a total of 108 pH determinations, the experimental error was only 0.001 pH (table 23), which corresponds closely with that obtained in Experiment 2. Likewise, the least highly significant mean difference in Experiment 3 was 0.029 pH which is almost the same as that found for Experiment 2 and close to that obtained in Experiment 1.

That the experimental error was consistently small is of a special interest when it is noted that these pH determinations were made at different times over a period of five and a half years.

## CONCLUSIONS

The results obtained in this study seem to warrant the following conclusions:

1. Five hundred pounds per acre or more of rock phosphate may be expected to neutralize a small part of the acidity of Carrington loam, Carrington silt loam, Grundy silt loam and Tama silt loam and may be expected to decrease the acidity of certain other soils to a small but measurable extent.
2. Sodium phosphate is more efficient in neutralizing acidity of Grundy silt loam than is rock phosphate applied in  $P_2O_5$  equivalent amounts.
3. An application of treble superphosphate equivalent to 300 pounds per acre of superphosphate may be expected to reduce some of the acidity of Carrington silt loam, Grundy silt loam and Tama silt loam and probably that of other soils but at this rate of application it is not as efficient a neutralizing agent as is a 500 pound application of rock phosphate.
4. Superphosphate, ammoniated phosphate and Ammo Phos "A" will increase the acidity of Carrington silt loam, Grundy silt loam and Tama silt loam slightly and may be expected to have a like effect on certain other acid soils.
5. There is an indication that rock phosphate may neutralize soil acidity sufficiently to produce a significant increase in the yield of sweet clover.
6. Although these changes in reaction resulting from phosphate fertilizers are highly significant statistically, they are too small to justify any conclusions as to their agricultural importance without further studying their effects on field crops growing in the field under ordinary farming conditions.

## SUMMARY

Studies were made of the effect of different phosphate fertilizers on the reaction of Carrington loam, Carrington silt loam, Tama silt loam and Grundy silt loam. The soils were sieved, treated with different phosphate fertilizers and with lime, mixed well, potted and kept in the greenhouse under uniform conditions. Changes in reaction were measured periodically by the quinhydrone electrode method, the Hardy and Lewis lime requirement method and by determining base exchange properties. In an attempt to isolate and evaluate the importance of the changes in reaction produced by the different treatments the effect of rock phosphate and sodium phosphate alone and in combination with lime and of lime alone on the content of exchangeable calcium, available phosphorus, and nitrate-nitrogen of Grundy silt loam was determined as well as the effect of these treatments on the yield and calcium content of two crops of sweet clover. The results of these studies may be summarized as follows:

1. The alcoholic-KOH method for determining replaceable calcium in high-lime soils seems more reliable than the ammonium acetate method.
2. Superphosphate, rock phosphate, sodium phosphate and lime at ordinary rates of application did not cause significant changes in the base exchange capacity of Grundy silt loam or Carrington silt loam.
3. Applications of 500 pounds per acre of finely ground rock phosphate produced highly significant decreases in the acidity of

Grundy silt loam, Carrington loam, Carrington silt loam and Tama silt loam.

4. The neutralizing effect of finely ground rock phosphate increased with increased rates of application.

5. Sodium phosphate was more efficient in neutralizing acidity of Grundy silt loam than was rock phosphate applied in equivalent amounts on the basis of  $P_2O_5$  content.

6. Treble superphosphate neutralized the acidity of Grundy silt loam, Carrington silt loam and Tama silt loam to a highly significant amount, but not to as large an extent as did rock phosphate.

7. The neutralizing effect of treble superphosphate increased with increasing rates of application.

8. The phosphate fertilizers studied were not as efficient as ground limestone or pure calcium carbonate in correcting soil acidity.

9. Three hundred pounds of superphosphate and equivalent amounts of ammoniated phosphate and Ammo Phos "A" resulted in highly significant increases in the acidity of Carrington silt loam, Grundy silt loam and Tama silt loam. Likewise, the acidity of Carrington loam was increased by applications of 120 and 240 pounds per acre of superphosphate.

10. Larger amounts of these materials caused further increases in acidity.

11. The effect of different phosphate fertilizers on soil reaction was found to vary somewhat with soil type.

12. The available phosphate content of Grundy silt loam increased with the rate of application of rock phosphate and of sodium phosphate.

13. Four tons per acre of calcium carbonate did not noticeably depress the amount of soluble phosphorus in the soil.

14. Finely ground rock phosphate caused highly significant increases in the yield of sweet clover on Grundy silt loam and there was a tendency for increased rates of application to produce higher yields.

15. There was a highly significant correlation between the pH of Grundy silt loam and the yield of sweet clover. Likewise, the treatments producing higher pH values consistently produced higher yields regardless of the amount of available phosphorus present.

16. There was evidence that decreased soil acidity resulting from applications of rock phosphate and sodium phosphate on Grundy silt loam was more important in increasing the yield of sweet clover than were the changes produced in the content of replaceable calcium, nitrate-nitrogen or available phosphorus in the soil.

17. Rock phosphate apparently has some value as a substitute for lime because it was found to neutralize acidity on certain Iowa soils to an extent which apparently resulted in significantly larger yields of sweet clover.

18. No evidence was found showing that rock phosphate could substitute for lime by supplying calcium to the plant. However, a high content of exchangeable calcium in the soil and a high per cent of calcium in the plant were associated with the highest

yields of sweet clover. Yet where phosphate fertilizers were added there was no measurable increase in these constituents. Further studies of the effect of phosphate fertilizers on the soluble calcium content of the soil are desirable.

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